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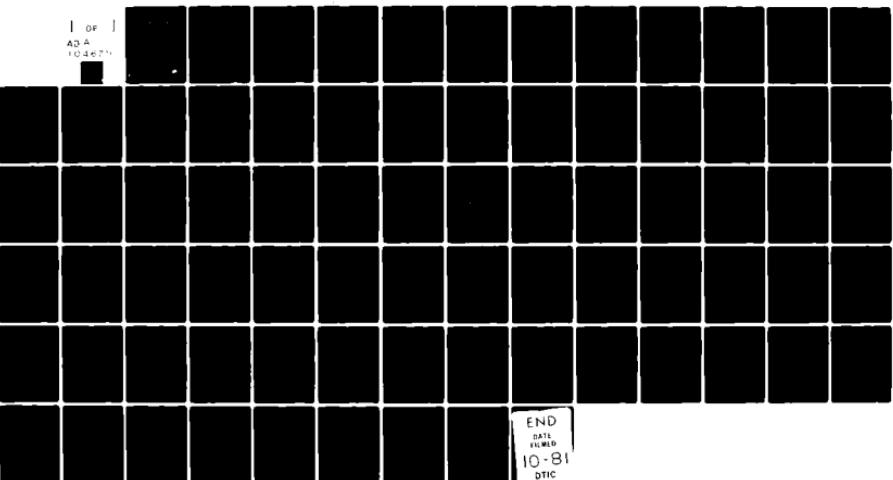
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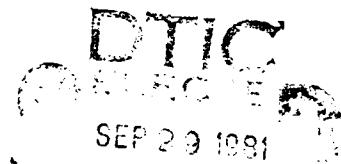
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## OPTOACOUSTIC SPECTROSCOPY TO DETECT HYDRAZINE FUELS

Edward S. Kolesar, Jr., Captain, USAF



July 1981

Final Report for Period 1 May 1979 - 1 February 1980

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USAF SCHOOL OF AEROSPACE MEDICINE  
Aerospace Medical Division (AFSC)  
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## NOTICES

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This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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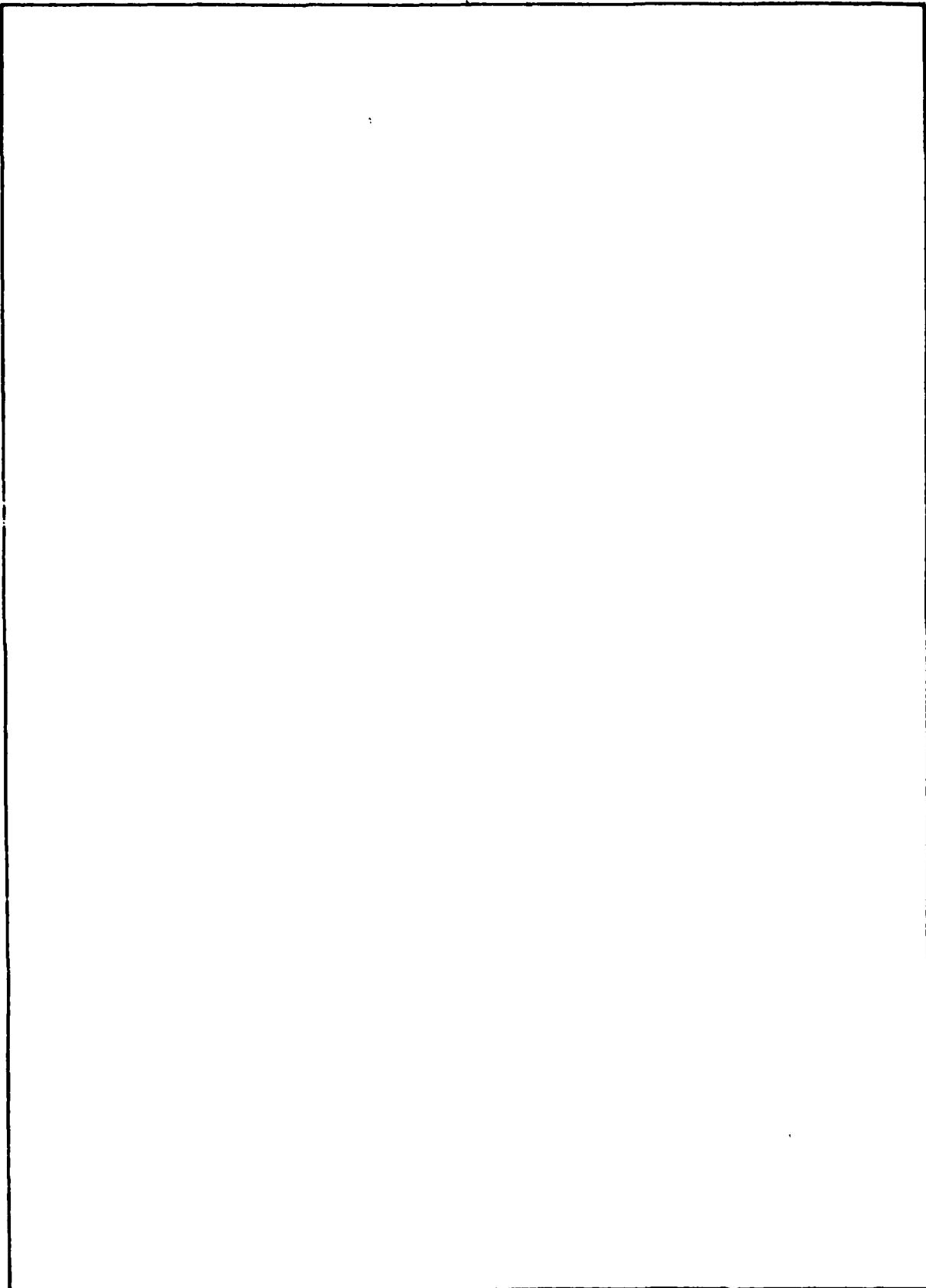
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## CONTENTS

	<u>Page</u>
INTRODUCTION . . . . .	3
BACKGROUND . . . . .	3
GENERAL SYSTEM DESCRIPTION . . . . .	7
Acoustic Signal Generation Process . . . . .	7
Acoustic Signal Detection . . . . .	18
OPTIMUM DESIGN OF AN OPTOACOUSTIC SPECTROMETER TO DETECT HYDRAZINE FUELS .	25
Laser Wavelength Selection . . . . .	27
Variable-Speed Chopper . . . . .	34
Microphone and Preamplifier . . . . .	34
Laser Power Meter . . . . .	35
Lock-In Amplifier . . . . .	35
Ratiometer . . . . .	38
Sample Cell Design . . . . .	39
CONCLUSION . . . . .	43
REFERENCES . . . . .	48

## FIGURES

### Fig. No.

1. Optoacoustic spectrometer equipment configuration . . . . .	8
2. Condenser microphone equivalent electrical circuit . . . . .	22
3. Condenser microphone and preamplifier equivalent electrical circuit noise model . . . . .	24
4. Hydrazine absorption spectra . . . . .	28
5. Monomethylhydrazine (MMH) absorption spectra . . . . .	29
6. Absorption spectra of 1,1-dimethylhydrazine (UDMH) . . . . .	30
7. Dimensional specifications for the Sylvania model 950A laser head, laser exciter, and model 750 cooling unit . . . . .	31
8. Conventional lock-in amplifier . . . . .	38
9. Nonresonant single-pass sample cell design . . . . .	45

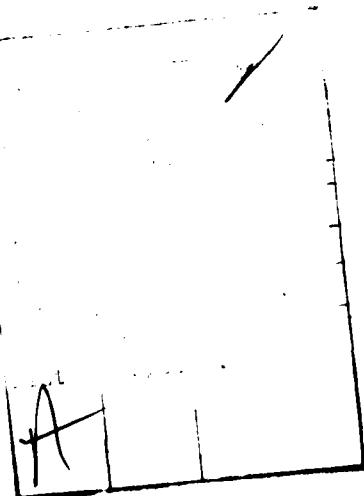
CONTENTS (Cont'd.)

<u>Fig. No.</u>		<u>Page</u>
10.	Optoacoustic spectrometer component integration for the measurement of the hydrazine fuels . . . . .	46

TABLES

Table No.

1.	Laser optoacoustic spectroscopy-detectable gas sensitivities (interference-free) . . . . .	4
2.	Technical characteristics of Sylvania model 950A CO <sub>2</sub> laser . . . . .	32
3.	Sylvania model 950A tunable laser wavelengths (00°1 - 10°0) band . .	33
4.	Technical characteristics of Brue & Kjaer model 4144 air condenser microphone . . . . .	36
5.	Technical characteristics of Brue & Kjaer model 2619 preamplifier and model 2804 power supply . . . . .	37
6.	Technical characteristics of Coherent Radiation model 210 laser power meter . . . . .	37
7.	Technical characteristics of Princeton Applied Research Corporation model 124A lock-in amplifier and model 117 preamplifier . . . . .	39
8.	Technical characteristics of Princeton Applied Research model 188 precision digital ratiometer . . . . .	40
9.	Summary of optimum design parameters for a hydrazine fuel opto-acoustic spectrometer . . . . .	44
10.	Relative optoacoustic spectrometer equipment costs . . . . .	47



## OPTOACOUSTIC SPECTROSCOPY TO DETECT HYDRAZINE FUELS

### INTRODUCTION

The U.S. Air Force now has need of a portable real-time point detector, with a sensitivity of at least 0.1 ppm, for the hydrazine fuels. Therefore the purpose of this report is to present the principles and practice of optoacoustic spectroscopy and a theoretical analysis of the feasibility for using this technique to detect the gaseous hydrazine fuels (hydrazine, monomethylhydrazine {MMH}, and 1,1-dimethylhydrazine {UDMH}). The success of numerous efforts to detect small quantities of gaseous pollutants is shown in Table 1.

### BACKGROUND

The optoacoustic effect was discovered by Alexander Graham Bell over 90 years ago (30-32). In his pioneering experiments, Bell focused mechanically chopped, non-dispersed sunlight onto a sample tube. When the light fell intermittently on a solid or liquid in the sample tube and was absorbed, Bell witnessed a "sonorousness" through an attached listening tube (a short length of tubing connected to one end of the sample cell, with the other end placed in the observer's ear). The frequency of the emitted sound was that at which the incident light was modulated.

The transformation of optic to acoustic energy was reported: "...the pulses of absorbed optical quanta are degraded in the sample to heat pulses, which in a gas, express themselves as pressure pulses, that is, sound...."(32). In summarizing the sonorous effects produced in a variety of materials, Bell prophesied: "I recognize the fact that the spectrophone must ever remain a mere adjunct to the spectroscope; but I anticipate that it has a wide and independent field of usefulness in the investigation of absorption-spectra in the ultra-red" (32).

Mercadier, Preece, Roentgen, and Tyndall also reported studies of the optoacoustic effect, particularly with gases (216, 285, 298, 299, 357). Their attempts were not very successful, due to the lack of sensitive acoustic detection devices. After these early studies, no further work was reported until 1938.

In 1938, three independent investigators reported the application of the optoacoustic effect to gas analysis. Luft, Pfund, and Veingerov all described instruments for the analysis of gases and gas mixtures which utilized the optoacoustic effect to detect their absorption of infrared radiation (196, 273, 360-362).

Since then, numerous investigators have measured the vibrational relaxation rates in gases, and have presented theoretical treatments of the optoacoustic effect (4, 6, 7, 11, 12, 16, 20-27, 42, 43, 45, 47-52, 54-56, 58, 60, 61, 64, 65, 69-71, 75, 77, 80, 91, 92, 94, 95, 106, 107, 110-113, 115, 118, 119, 124, 125, 136, 148-154, 158, 160, 163, 167, 173-178, 181, 185, 188, 194, 202-205,

TABLE 1. LASER OPTOACOUSTIC SPECTROSCOPY-DETECTABLE GAS SENSITIVITIES (INTERFERENCE-FREE)

<u>Gas</u>	<u>Laser</u>	<u>Wavelength (<math>\mu\text{m}</math>)</u>	<u>Sensitivity (ppb)</u>	<u>Reference</u>
Acetonitrile	$\text{CO}_2$	9.4 P(16)	670.0	252
Acetylene	$\text{CO}_2$	10.4 P(14)	3.0	252
Ammonia	$\text{CO}_2$	10.4 R(6)	5.3	252
	$\text{CO}_2$	9.4 R(30)	0.8	252
	$\text{CO}_2$	10.7 P(32)	1.2	204
	$\text{CO}_2$	6.2 P(15)	0.4	176
	$\text{CO}_2$	9.2 R(30)	0.3	318
	$\text{CO}_2$	10.4 R(6)	1.1	318
Benzene	$\text{CO}_2$	9.4 P(30)	48.0	252
	$\text{CO}_2$	9.4 P(20)	143.0	252
	$\text{CO}_2$	9.6 P(30)	3.0	176
1,3-Butadiene	CO	6.2 P(13)	1.0	175
	$\text{CO}_2$	10.7 P(30)	2.0	176
Butane	$\text{CO}_2$	10.4 R(14)	200.0	252
T-Butanol	$\text{CO}_2$	10.4 P(34)	26.0	252
	$\text{CO}_2$	10.4 P(30)	31.0	252
1-Butene	CO	6.1 P(9)	2.0	175
	$\text{CO}_2$	10.8 P(38)	2.0	176
Cyclohexane	$\text{CO}_2$	9.4 P(28)	250.0	252
Cyclohexanone	$\text{CO}_2$	9.6 P(10)	20.2	71
1,2-Dichloroethane	$\text{CO}_2$	10.4 P(10)	450.0	252
	$\text{CO}_2$	10.4 P(22)	500.0	252
Dinitrate	$\text{CO}_2$	9.6 P(14)	8.26	71
2,4-Dinitrotoluene	$\text{CO}_2$	9.6 P(16)	0.5	71
Ethyl Acetate	$\text{CO}_2$	9.4 P(6)	8.3	252
	$\text{CO}_2$	9.4 P(14)	9.0	252
Ethylene	$\text{CO}_2$	10.4 P(14)	2.6	252
	$\text{CO}_2$	10.5 P(14)	0.2	176
	$\text{CO}_2$	10.5 P(14)	0.3	177
	$\text{CO}_2$	10.5 P(14)	0.3	330
Ethylene Glycol	$\text{CO}_2$	9.4 P(14)	38.0	252
Freon-11	$\text{CO}_2$	9.4 R(22)	18.0	252
Freon-12	$\text{CO}_2$	9.4 R(20)	20.0	252
	$\text{CO}_2$	10.4 P(30)	5.5	252
	$\text{CO}_2$	10.8 P(42)	0.35	318
	$\text{CO}_2$	9.2 R(32)	2.4	318

(Cont'd. on facing page)

TABLE I. (Cont'd.)

<u>Gas</u>	<u>Laser</u>	<u>Wavelength (<math>\mu\text{m}</math>)</u>	<u>Sensitivity (ppb)</u>	<u>Reference</u>
Freon -113	$\text{CO}_2$	9.4 P(26)	5.0	252
Freon -114	$\text{CO}_2$	9.4 P(14)	3.6	252
Furan	$\text{CO}_2$	10.4 R(30)	25.0	252
Iodo Propane	$\text{CO}_2$	9.4 R(24)	360.0	252
Isopropanol	$\text{CO}_2$	10.4 P(10)	29.0	252
Methane	He-Ne	3.4	10.0	174
Methanol	$\text{CO}_2$	9.7 P(34)	0.3	176
Methyl Chloroform	$\text{CO}_2$	9.4 R(24)	11.0	252
Methyl Ethyl Ketone	$\text{CO}_2$	10.4 P(22)	83.0	252
Methylamine	$\text{CO}_2$ $\text{CO}_2$	9.4 P(24) 9.6 P(30)	120.0 25.3	252 71
Nitric Oxide	CO CO	5.2 P(11) 5.3 P(12)	0.4 10.0	176 175
Nitrogen Dioxide	CO Dye Argon	6.2 P(14) 0.5 ~ 0.6 Not reported	0.1 4.0 5.0	176 64 137
Nitroglycerine	$\text{CO}_2$ $\text{CO}_2$	9.4 P(14) 9.4 P(14)	0.7 0.23	252 71
Ozone	$\text{CO}_2$	9.4 P(14)	9.0	252
Perchloroethylene	$\text{CO}_2$ $\text{CO}_2$ $\text{CO}_2$ $\text{CO}_2$	10.4 P(42) 10.4 P(40) 10.8 P(42) 10.8 P(40)	3.2 4.3 1.1 1.4	252 252 318 318
Propylene	CO	6.1 P(9)	3.0	176
Sulfur Hexafluoride	$\text{CO}_2$	10.4 P(16)	0.2	252
Trichloroethylene	$\text{CO}_2$ $\text{CO}_2$ $\text{CO}_2$	10.4 P(20) 10.6 P(24) 10.6 P(20)	13.0 0.7 4.2	252 176 318
Vinyl Chloride	$\text{CO}_2$	10.4 P(22)	12.0	252
Water	CO	5.9 P(13)	14.0	176

207, 208, 209, 211, 212, 228, 235, 240, 246, 255, 257, 259, 262-268, 270, 271, 286, 287, 292, 294, 295, 297, 300, 303, 313-315, 318-320, 322, 330, 336, 342-345, 347, 351-356, 365-368, 370-373, 379, 381-383, 387). Refinements in the instrumentation used for optoacoustic measurements have also been reported (1, 4, 5, 9, 18, 20, 22, 24, 35-39, 41, 42, 44, 46, 54, 55, 62, 63, 66, 67, 73, 74, 78, 79, 81, 82, 84, 85, 90, 93, 96-101, 103, 104, 114, 116, 117, 120-123, 131, 132, 137, 145, 146, 149, 156, 157, 162, 168-172, 179, 180, 186, 187, 190, 193, 197, 199-202, 215, 220, 224-227, 229, 236-239, 241, 243-245, 248, 249, 252, 253, 260, 261, 269, 272, 274-276, 278, 279, 287-291, 293, 301, 302, 304, 321, 332, 334, 337, 338, 341, 348-350, 359, 364, 376, 385, 386).

In addition to studying gases by optoacoustic spectroscopy, many investigators have applied this technique to the direct examination of solid and semi-solid samples (3, 8-10, 13-15, 17, 19, 33-39, 53, 57, 12, 76, 83, 86, 114, 126-130, 133-135, 155, 159, 161, 164, 166, 182, 183, 191, 192, 195, 198, 206, 210, 213, 217, 223, 230-234, 247, 254, 258, 277, 296, 305-312, 316, 317, 333, 335, 340, 346, 363, 369, 374, 378, 380, 384). Houghton and Acton observed optoacoustic signals from films of acetylene soot, camphor soot, flat-black paper, and black-body cavities (133). Marshbarger and Robin, who described an experimental configuration for optoacoustic spectroscopy in the UV and the visible region, reported its application in analyzing various solid samples--including powdered K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, flower petals, grass, dried blood smears, ultramarine, and carbon black (118). Rosencwaig described the use of optoacoustic spectroscopy to obtain spectra for inorganic samples and biological materials (304-312). Parker (258) and Parker and Ritke (259) observed optoacoustic signals from a surface film on the window of a sample cell designed to study the collisional deactivation of singlet molecular oxygen. Bennett and Forman (33-39), Kerr (159), Kerr and Atwood (160), and Rosencwaig and Gersho (310, 311) developed not only theoretical interpretations of the optoacoustic effect observed in sample cells excited by laser or continuum sources but also theoretical explanations for the heat transfer process at the solid-gas interface. The measurement and theory of thermal diffusivity and optical absorption spectra, particularly for nonhomogeneous samples, have also been documented (14, 16, 27, 28, 33-39, 48, 52, 56, 60, 61, 69, 70, 75, 77, 80, 81, 91, 92, 94, 112, 113, 115, 118, 119, 122, 126-130, 133, 134, 155, 159, 160, 164, 166, 171, 173, 174, 177, 181-183, 185, 188, 191, 192, 195, 196, 205-208, 210-212, 217, 223, 234, 247, 256, 258, 259, 262, 265, 267, 296, 297, 300, 310, 311, 313, 316, 317-319, 330, 334-336, 340, 345, 351, 353-356, 360-362, 365, 366, 370, 372, 378, 382, 384).

One of the most recent applications of optoacoustic spectroscopy has been the detection of asbestos fibers (chrysotile) in municipal drinking water at concentrations as low as 0.1 nanograms per cubic centimeter (277). Also, the General Motors Research Laboratory has fabricated an optoacoustic spectrometer to measure diesel engine exhaust particulate emissions with a 0.5-sec response time (254, 275, 276).

In brief, according to the foregoing review of the development and application of optoacoustic spectroscopy, its use in gaseous and in solid analyses has been established and accelerated with the introduction of laser sources.

## GENERAL SYSTEM DESCRIPTION

In optoacoustic spectroscopy, radiant light energy (watts) is first converted to sound pressure (pascals), and then to an electrical potential (volts). Figure 1 represents a simplified experimental optoacoustic spectroscopy system. Light from the laser is modulated by passing it through a rotating mechanical chopper. The modulated beam then passes through a container that holds a gas sample. Energy absorbed from the laser beam heats the gas and causes its pressure to rise. Since the beam is modulated, this pressure rise is periodic at the beam modulation frequency. The periodic pressure fluctuations are detected by a microphone, converted to an electrical signal, and amplified by the pre-amplifier. The detector at the exit of the optoacoustic cell is used to sample the laser beam so that compensation can be made for variations in the optoacoustic spectra caused by wavelength and temporal intensity fluctuations of the laser emission. The two synchronized lock-in amplifiers in the signal-processing section compensate for phase changes due to laser beam walking, since a mechanical chopper with narrow slits converts beam walking to phase changes. Compensation for the aforementioned effects is accomplished by ratioing, with the ratiometer, the outputs of the lock-in amplifiers. The optoacoustic spectra are usually recorded on a strip-chart recorder for subsequent analysis.

## Acoustic Signal Generation Process

In order to maximize the sensitivity of an optoacoustic system and enhance its trace gas detection capabilities, one must understand the acoustic signal generation process and the variables affecting it.

The first step in the generation of an optoacoustic signal is the absorption of energy from the modulated laser beam. This absorbed energy produces a periodically varying heat disturbance in the gas and becomes the source of sound energy. A theoretical analysis of the acoustic signal generation process has been developed by Rosengren (313, 314) and by others (7, 8, 11, 12, 14-16, 33-35, 39, 42, 70, 77, 80, 113, 150, 152, 155, 160, 173-176, 191, 203, 204, 206, 208, 211, 212, 230-232, 240, 242, 256, 287, 306-308, 352, 354, 368). The important descriptive relationships are summarized here:

The intensity of a laser beam ( $\text{erg}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ ) can be expressed as  $I(\vec{r},t)$ , where  $\vec{r}$  describes position and  $t$  is time. The heat disturbance produced by the beam can be represented as  $H(\vec{r},t)$ .  $H$  has dimensions of power per unit volume ( $\text{erg}\cdot\text{cm}^{-3}\cdot\text{sec}^{-1}$ ). For many experimental situations,  $H$  and  $I$  are related by a simple proportionality constant ( $\alpha$ ):

$$H = \alpha I \quad (1)$$

The constant ( $\alpha$ ) has dimensions of reciprocal length ( $\text{cm}^{-1}$ ) and is commonly referred to as absorbance. Equation 1 is valid when the two following conditions are satisfied:

- a. The intensity ( $I$ ) is sufficiently small so that the absorbing transition is not saturated.

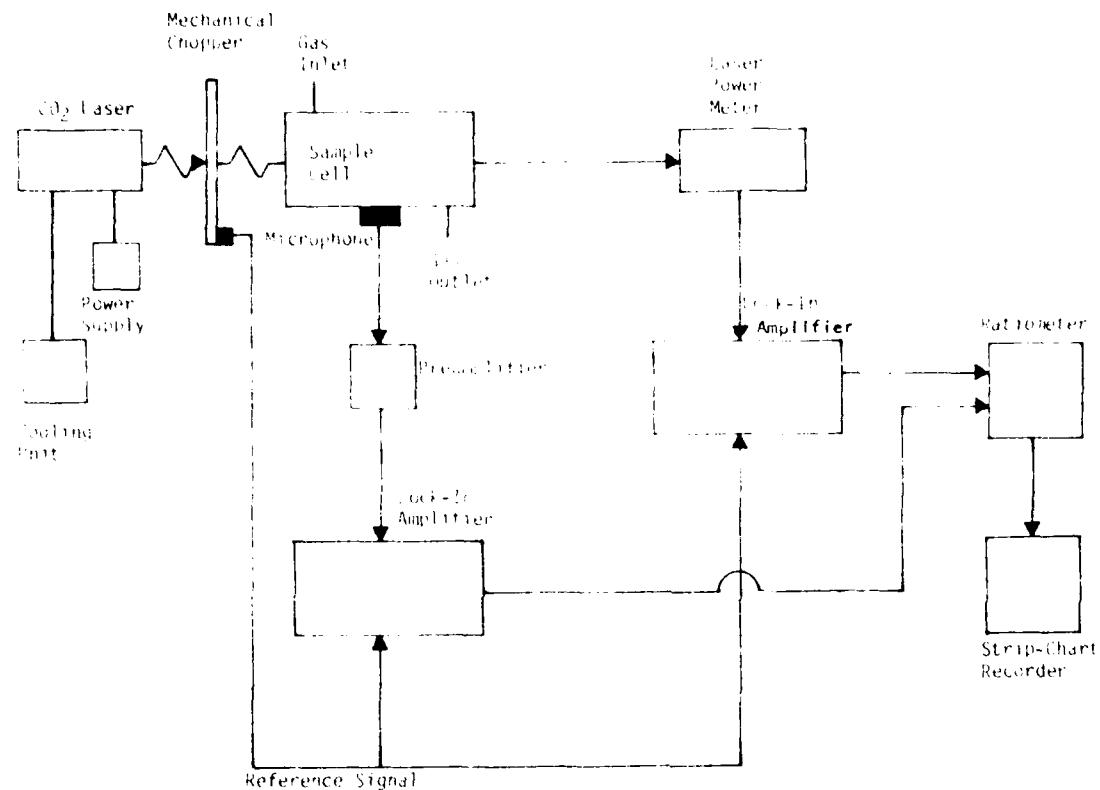


Figure 1. Optoacoustic spectrometer equipment configuration.

- b. The time variation of  $I$  is much slower than the transfer rate of absorbed energy responsible for producing heat.

If either or both conditions are not satisfied, the relationship between  $n$  and  $I$  becomes complex, and quantum mechanical coherent effects must be considered. For situations when the two foregoing conditions (a and b) have been satisfied, however, a rate equation relating  $\dot{N}$  and  $I$  has been developed by Kaiser (15d) and Kruezer (175-176).

To illustrate the rate equation, let  $N$  be the density of absorbing molecules;  $n_1$ , the density of absorbing molecules in the excited state;  $h\nu$ , the energy of the transition;  $\Delta\nu$ , the line width of the transition;  $S$ , the line strength of the transition;  $\tau_R$ , the radiative lifetime; and  $\tau_C$ , the collisional decay time of the upper state. The equation describing the upper-state population for paths of decay which are radiative and collision-induced is:

$$\frac{dn_1}{dt} = (-n_1) \left[ \frac{I}{h\nu} \left( \frac{S}{\pi\Delta\nu} \right) + \frac{\tau_C^{-1}}{\tau_R} + \tau_C^{-1} \right] + (N-n_1) \left( \frac{I}{h\nu} \right) \left( \frac{S}{\pi\Delta\nu} \right) \quad (2)$$

Under normal circumstances, collisional excitation effects in the upper state are neglected; this assumption is valid as long as  $h\nu \gg kT$ , where  $k$  is Boltzmann's constant and  $T$  is the gas temperature.

The solution of Equation 2 yields the dependence of the upper state population on light intensity ( $I$ ), density of absorbing molecules ( $N$ ), and various parameters that describe the transition. The time dependence of  $I$  can be expressed as:

$$I(t) = I_0 [1 + f(t)], \quad (3)$$

where  $I_0$  is a constant. Thus, a solution to Equation 2 is:

$$\begin{aligned} \frac{n_1(t)}{N} &= (D/F) + (2FT)^{-1} \left\{ 1 - F \exp \left\{ - \int_0^t [F + 2Df(t')] dt' \right. \right. \\ &\quad \left. \left. \cdot \int_0^{t'} \exp \left\{ \int_0^{t''} [F + 2Df(t'')] dt'' \right\} dt' \right\} \right\} \end{aligned} \quad (4)$$

The spontaneous decay rate of the upper state ( $\tau^{-1}$ ) is given by:

$$\tau^{-1} = \tau_R^{-1} + \tau_C^{-1} \quad (5)$$

The stimulated rate ( $D$ ) for absorption or emission of radiation, is given by:

$$D = I_0 S / (\hbar v \pi \Delta v) \quad (6)$$

and the quantity  $F$  is defined as:

$$F = 2D + \tau^{-1} \quad (7)$$

The solution to Equation 2, which gives the upper-state population density, can be simplified if the time variation of  $I(t)$  is sufficiently slow. In particular, if the time variation of  $I(t)$  is slow compared to that of  $F$ , then the left side of Equation 2 can be set equal to zero. Under this condition, a solution for  $n_1$  is:

$$\frac{n_1}{N} = \frac{(IS/\hbar v \pi \Delta v)}{(2IS/\hbar v \pi \Delta v) + \tau^{-1}} \quad (8)$$

Equation 8 shows the transition saturation effect for large  $I$ , that is,  $(2IS/\hbar v \pi \Delta v \gg \tau^{-1})$ ; and in the limit of large  $I$ ,  $(n_1/N)$  becomes equal to  $(1/2)$ , and the absorbing molecules are evenly divided between the upper and lower states of the transition. In the limit for small  $I$ , Equation 8 reduces to:

$$\left(\frac{n_1}{N}\right) \approx \left(\frac{IS\tau}{\hbar v \pi \Delta v}\right) \quad (9)$$

Thus, when the time variation of  $I$  is sufficiently slow, and the intensity sufficiently weak,  $n_1$  is proportional to  $I$ .

Heat is generated in the gas by the nonradiative decay of the excited state population ( $n_1$ ). The rate of heat generation is given by:

$$H = (n_1/\tau_C) \hbar v \quad (10)$$

For those cases where Equation 8 is a good approximation, Equations 9 and 10 can be combined to yield a linear dependence of  $H$  on  $I$ . The result is:

$$\alpha = \frac{NSI}{\pi \Delta v \tau_C} \quad (11)$$

Thus, the absorbance ( $\alpha$ ) is defined as a function of the constants describing the transition process. The optoacoustic absorbance given by Equation 11 describes the conversion of light energy into heat.

The second step in the generation of the optoacoustic signal is the excitation of sound in the gas. The detailed theoretical treatment of this process has been developed by various investigators (7, 8, 11, 12, 14-16, 33-35, 39, 42, 70, 71, 80, 113, 150, 152, 155, 160, 173-176, 191, 203, 204, 206, 208, 211, 212, 230-232, 240, 256, 287, 306-308, 313, 314, 352, 354, 368). The excitation process for acoustic normal modes in a sample cell, the calculation of the quality factor for these modes, and the generation of noise by thermal fluctuations are summarized in the following:

Sound in the gas can be described by the acoustic pressure  $p(\vec{r}, t)$ , which is the difference between the total pressure  $P$ , and its average value,  $P_0$ :

$$p = P - P_0 \quad (12)$$

Morse and Ingard (228) have shown there is an acoustic velocity  $\{\vec{u}(\vec{r}, t)\}$  and temperature  $\{T(\vec{r}, t)\}$  associated with the acoustic pressure ( $p$ ). The acoustic velocity is the fluid velocity of the gas at position  $\vec{r}$  and time  $t$  caused by the sound. The acoustic temperature is the departure from the average temperature ( $T$ ) caused by the sound.

The heat  $\{H(\vec{r}, t)\}$ , produced by the absorption of light, acts as a source for the generation of sound (228). This effect can be described by:

$$\nabla^2 p - c^{-2} (\partial^2 p / \partial t^2) = - [(\gamma - 1)/c^2] (\partial H / \partial t) \quad (13)$$

where  $c$  is the velocity of sound, and  $\gamma$  is the ratio of the specific heat of the gas at constant pressure ( $C_p$ ) to that at constant volume ( $C_v$ ).

Equation 13 is an inhomogeneous wave equation that can be solved by taking the Fourier transform of both sides, and expressing the solution ( $p$ ) as an infinite series expansion of the normal mode solutions ( $p_n$ ) of the homogeneous wave equation (173, 174, 226-228, 256). The Fourier transform of Equation 13 yields:

$$(\nabla^2 + \omega^2/c^2)p(\vec{r}, \omega) = [(\gamma - 1)/c^2] i\omega H(\vec{r}, \omega) \quad (14)$$

where

$$p(\vec{r}, t) = \int p(\vec{r}, \omega) e^{-i\omega t} d\omega \quad (15)$$

$$H(\vec{r}, t) = \int H(\vec{r}, \omega) e^{-i\omega t} d\omega \quad (16)$$

The normal mode solutions for a homogeneous wave equation are determined by the boundary conditions. If the walls of the sample cell are rigid, the acoustic velocity component normal to the wall must vanish at the wall. Since the acoustic velocity ( $\dot{u}$ ) is related to the gradient of  $p$  in the following relationship ( $\rho$  is density):

$$\dot{u}(\vec{r}, \omega) = (i\omega\rho_0)^{-1} \nabla \cdot \vec{p}(\vec{r}, \omega) \quad (17)$$

it follows that the gradient of  $p$  normal to the boundary must vanish at the boundary (173, 174, 228, 256). This boundary condition determines the normal mode solutions ( $p_j$ ) of the homogeneous wave equation:

$$(\nabla^2 + k_j^2)p_j(\vec{r}) = 0 \quad (18)$$

If the resonant frequency of the normal mode ( $p_j(\vec{r})$ ) is set equal to  $\omega_j$ , these modes will be orthogonal and may be normalized with the normalization condition given by (173, 174, 226-228, 256):

$$\int p_j^* p_j dV = V_C \delta_{kj} \quad (19)$$

The volume integral is over the sample cell volume ( $V_C$ ).

For a sample cell cylinder of radius  $a$ , and length  $\ell$ , Equation 18 can be written in cylindrical coordinates (173, 174, 226-228, 256):

$$\vec{r}^{-1} \frac{\partial}{\partial \vec{r}} (\vec{r} \frac{\partial p_j}{\partial \vec{r}}) + \vec{r}^{-2} \frac{\partial^2 p_j}{\partial \phi^2} + \frac{\partial^2 p_j}{\partial z^2} + p_j \frac{\omega_j^2}{c^2} = 0 \quad (20)$$

Morse (226) Morse and Ingard (227, 228) found a solution given by:

$$p_j = \frac{\cos(m\phi)}{\sin(m\phi)} [A J_m(k_r \vec{r}) + B N_m(k_r \vec{r})] [C \sin(k_z z) + D \cos(k_z z)] \quad (21)$$

where  $J_m$  and  $N_m$  are Bessel functions of the first and second kind, respectively. Since  $N_m$  becomes infinite as  $\vec{r}$  approaches zero, it follows that  $B = 0$ , if Equation 20 is to represent the pressure inside a cylindrically-shaped sample.

cell. To satisfy the boundary condition imposed by rigid sample cell walls, the gradient of  $p$  normal to the cell walls must vanish at the walls. If one end of the gas container is set at  $z = 0$ , and the other end is at  $z = \ell$ , it follows that  $C = 0$ , and the allowed values of  $k_z$  are given by:

$$k_z = (\pi/\ell)n_z \text{ for } (n_z = 1, 2, 3, \dots) \quad (22)$$

Applying the same boundary condition to the walls at  $\vec{r} = a$ , leads to the condition that the derivative of  $J_m(k_r \vec{r})$ , with respect to  $\vec{r}$ , must vanish at  $\vec{r} = a$ :

$$\left[ \frac{d J_m(k_r \vec{r})}{d \vec{r}} \right] \Bigg|_{\vec{r} = a} = 0 \quad (23)$$

which is equivalent to the general expression developed by Morse (226) and Morse and Ingard (227, 228):

$$\left[ \frac{d J_m(\pi \alpha)}{d \alpha} \right] \Bigg|_{\alpha = \alpha_{mn}} = 0 \quad (24)$$

$$\text{for } k_r = \pi \alpha_{mn}/a \quad (25)$$

where  $\alpha_{mn}$  is the  $n^{\text{th}}$  root of the equation involving the  $m^{\text{th}}$  order Bessel function. The requirement that  $p$  be continuous, limits  $m$  to integral values. Substituting Equation 21 into Equation 20 yields the resonant frequency of the mode:

$$\omega_j = c [k_z^2 + k_r^2]^{1/2} \quad (26)$$

Thus the acoustic pressure ( $p$ ) can be expressed as an expansion of the normal mode pressure components ( $p_j$ ) and their associated amplitude components ( $A_j$ ):

$$p(\vec{r}, \omega) = \sum_j A_j(\omega) p_j(\vec{r}) \quad (27)$$

Substituting Equation 27 into Equation 13 yields:

$$A_j(\omega) = - \left( \frac{i\omega}{\omega_j^2} \right) \frac{[(\gamma - 1)/V_C] \int p_j^* H dV}{(1 - \omega^2/\omega_j^2)} \quad (28)$$

which gives the mode amplitude components (173, 174, 226-228, 256). The integral in the numerator on the right side of Equation 28 represents the coupling between the heat disturbance ( $H$ ) and the normal mode pressure components ( $p_j$ ). The denominator represents the mode resonance with  $A_j$ , and becomes infinite as  $\omega$  approaches the natural resonant frequency  $\omega_j$ . This physically unreasonable situation is the result of the absence of any loss mechanism in Equation 13. A correction can be made by modifying Equation 28 to include mode damping described by the quality factor ( $Q_j$ ) (173, 174, 226-228, 256):

$$A_j(\omega) = - \left( \frac{i\omega}{\omega_j^2} \right) \frac{[(\gamma - 1)/V_C] \int p_j^* H dV}{[1 - \omega^2/\omega_j^2 - i\omega/\omega_j Q_j]} \quad (29)$$

A method for calculating  $Q_j$  from the undamped function,  $p_j$ , follows:

To show the explicit dependence of the acoustic signal on the gas absorption and light intensity,  $H$  must be replaced in Equation 29. Using Equation 1, the substitution yields:

$$A_j(\omega) = - \left( \frac{i\omega}{\omega_j^2} \right) \frac{\alpha[(\gamma - 1)/V_C] \int p_j^* I dV}{[1 - \omega^2/\omega_j^2 - i\omega/\omega_j Q_j]} \quad (30)$$

Two cases should be considered for Equation 30. First,  $I$  is assumed a constant throughout the volume of the container. In this case, the integral in the numerator of Equation 28 vanishes for  $j \neq 0$ . The lowest order mode ( $p_0$ ) has a resonant frequency ( $\omega_0 = 0$ ), and represents a constant pressure change in the container. In this particular case,  $I$  and  $p_0$  are proportional to each other, and the vanishing of the integral for  $j \neq 0$  is a direct result of the orthogonality of the functions for  $p_j$ . Under these conditions, Equation 30 reduces to:

$$A_0(\omega) = \frac{i \alpha (\gamma - 1) I}{\omega [1 + (i/\omega T)]} \quad (31)$$

The time ( $\tau_T$ ), in the denominator of Equation 31, is the damping time for  $p_0$  resulting from heat conduction from the gas to the container walls. Assuming that the gas container is cylindrical in shape with a cross sectional area ( $A_C$ ), length ( $\ell$ ), and volume ( $V_C$ ), the total light beam power ( $W$ ) is equal to  $IV_C/\ell$ . In Equation 31 the intensity ( $I$ ) can be replaced by  $W\ell/V_C$ , to yield:

$$A_0(\omega) = \frac{i\alpha(\gamma - 1) W\ell}{\omega(1 + i/\omega\tau_0)V_C} \quad (32)$$

For the second case, the situation is considered where the spatial distribution of the intensity is adjusted so that only the first-order mode ( $p_1$ ) is excited. Equation 30 reduces to:

$$A_1(\omega) = - \left( \frac{i\omega}{\omega_1^2} \right) \frac{\alpha(\gamma - 1) W\ell}{V_C [1 - (\omega^2/\omega_1^2) - i(\omega/\omega_1 Q_1)]} \quad (33)$$

Exciting a resonant mode ( $i \neq 0$ ) has distinct advantages. At low frequencies ( $\omega\tau_T \ll 1$ ), the zero-order mode amplitude is constant, is independent of frequency, and has the value:

$$A_0 = \frac{\alpha(\gamma - 1) W\ell\tau_T}{V_C} \quad (34)$$

At high frequencies ( $\omega\tau_T \gg 1$ ), the amplitude decreases as  $1/\omega$ . The first-order mode amplitude reaches a maximum at  $\omega = \omega_1$ . The ratio of the maximum amplitude of the first resonant mode to that of the zero-order mode is:

$$A_1(\omega_1)/A_0(0) = Q_1/\omega_1\tau_1 \quad (35)$$

If the value of this ratio is greater than unity, then the first-order mode amplitude is larger than the zero-mode amplitude. Thus, the value of this ratio depends on mode damping.

Calculation of the quality factor ( $Q$ ) can be accomplished by separating the viscosity and heat conduction losses into a volume and surface loss (228). The surface loss occurs in a thin region near the walls. This region can be considered to consist of two layers that extend out from the wall of the cell. One layer is of thickness  $\delta_V$ , in which the viscosity effects take place; and the

other, of thickness  $\ell_h$ , in which heat conduction effects occur. The associated skin depths are (173, 174, 226-228, 256):

$$\ell_v = 2\eta/\omega \rho_0 c_p \quad (36)$$

$$\ell_h = 2k/\nu_0 \omega C_p \quad (37)$$

where  $\eta$  is the viscosity and  $k$  is the thermal conductivity of the gas. The total surface loss ( $L_{sj}$ ) is given by:

$$L_{sj} = |A_j|^2 \int [1/2 R_v |\dot{u}_{tj}|^2 + 1/2 R_h |p_j|^2] dS \quad (38)$$

where  $\dot{u}_{tj}$  is the acoustic velocity component tangent to the cell's walls, and  $R_v$  and  $R_h$ , representing the loss from viscosity and heat conduction, are given by (173, 174, 226-228, 256):

$$R_v = (\eta \omega \rho_0 / 2)^{1/2} \quad (39)$$

$$R_h = [(Y - 1)/\rho_0 c^2] (\kappa \omega / 2 \rho C_v)^{1/2} \quad (40)$$

The volume loss ( $L_{vj}$ ) is given by:

$$L_{vj} = (\omega_j^2 / \rho^2 c^4) [ (Y - 1)(\kappa / 2 C_p) + (2\eta / 3) |V_C| |A_j|^2 ] \quad (41)$$

The energy ( $E_j$ ) stored in mode  $j$  is given by:

$$E_j = V_C |A_j|^2 / \rho_0 c^2 \quad (42)$$

Therefore, the quality factor ( $Q_j$ ) can be calculated from Equations 39, 41, and 42, and the definition of  $Q$ :

$$Q_j = \omega_j \frac{\text{Energy Stored in Mode } j}{\text{Rate of Loss of Energy From Mode } j} \quad (43)$$

or

$$Q_j = \omega_j \left( \frac{E_j}{L_{sj} + L_{vj}} \right) \quad (44)$$

The acoustic normal modes of the gas-filled sample cell are also excited by thermal fluctuations, thus producing a noise source that causes a fundamental limitation on acoustic signal detection sensitivity. Kittel (165) has described the theory of thermal fluctuations. The power spectrum of the noise is given by:

$$|A_{jn}(\omega)|^2 = \frac{4\rho_0 c^2 kT}{V_C \omega_j Q_j \{(1-\omega^2/\omega_j^2)^2 + (\omega/\omega_j Q_j)^2\}} \quad (45)$$

Mode damping has an influence on thermal fluctuation noise. The total energy of excitation for a mode is equal to  $kT$ , and is not affected by  $Q_j$ . However, the frequency components of the noise depend on  $Q_j$ . Increasing  $Q_j$  shifts the noise into a narrow band around the mode resonant frequency. In the case where the signal frequency is well below the mode resonant frequency ( $\omega \ll \omega_j$ ), Equation 45 reduces to:

$$|A_{jn}(\omega)|^2 = 4\rho_0 c^2 kT / \omega_j Q_j V_C \quad (46)$$

This equation shows that noise may be reduced by increasing  $Q_j$ .

A useful quantity to evaluate the performance of a detector is the noise-equivalent-power (NEP). The NEP of an optoacoustic detector is the amount of power that would have to be absorbed by the gas to produce a signal amplitude equal to the noise amplitude given by Equation 45. For optoacoustic systems, the NEP is given by (40, 173, 174, 226-228, 256):

$$(NEP)' = 8\pi\rho_0 c^2 kTV_C \omega_j^2 / \omega_j Q_j (\gamma - 1)^2 \quad (47)$$

and has the units of power (watts) per square-root of frequency (hertz). The value of Equation 47 is that it can be used to optimize the design of an opto-acoustic system. It shows that the NLP is reduced by increasing the resonant frequency and  $\Omega$ .

### Acoustic Signal Detection

The final step in the generation of an optoacoustic signal is the detection of the acoustic excitation. The detector element most commonly used is the condenser microphone. In order to calculate the magnitude of the electrical signal produced by the microphone and compensate for the noise that will be added to this signal by the microphone and its associated preamplifier, one must develop the behavioral theory of the microphone in the context of an optoacoustic application (24, 29, 80, 102, 147, 173, 174, 180, 214, 218, 219, 230, 231, 240, 242, 256, 282, 291, 309, 313, 314, 327-329, 348, 377, 386). Treatment of the condenser microphone mechanically--in terms of position, mass, damping, and spring constant--has been documented by several investigators (29, 173, 174, 180, 230, 231, 240, 256, 313, 314). Also, an electrical model of the microphone--in terms of its equivalent circuit--has been developed; and a summary of this model follows here (173, 180, 256, 328, 329, 348, 386):

The condenser microphone diaphragm is usually fabricated from a thin metal disc that is mounted to produce a large radial tension. Acoustic pressure acting on one side of the diaphragm causes it to move. This motion is detected by a change in capacity between the diaphragm and a fixed plate, mounted behind the diaphragm. Motion of the diaphragm may be described by the modes of vibration for a thin plate. Since the lowest order modes will cause the greatest change in capacity, only these modes will be considered. The motion of the diaphragm that generates a signal can be described by a single degree of freedom, which corresponds to the diaphragm bending into a spherical shape. To illustrate, consider the diaphragm at rest in the  $yz$ -plane and its center at the origin. The lowest order mode corresponds to a displacement of each point of the diaphragm in the  $x$  direction by an amount,  $x(\vec{r})$ , given by:

$$x(\vec{r}) = x(0)[1 - \vec{r}^2/b^2] \quad (48)$$

where  $\vec{r}$  is the distance between the origin and any point on the diaphragm,  $x(0)$  is the displacement of the diaphragm at the origin, and  $b$  is the radius of the diaphragm. The average displacement of the diaphragm can be found by averaging  $x(\vec{r})$  over the diaphragm to yield:

$$x = (\pi b^2)^{-1} \iint x(\vec{r}) \vec{r} d\vec{r} d\Omega \quad (49)$$

Substituting Equation 48 into Equation 49 yields:

$$x = 1/2 [x(0)] \quad (50)$$

that is, the average displacement is one-half the displacement at the center. The lowest order mode equation of motion for the average coordinate  $x$  is:

$$m \frac{d^2x}{dt^2} + \delta \frac{dx}{dt} + K_m x = \vec{F} \quad (51)$$

where  $m$  is the mass of the diaphragm;  $\delta$ , the damping factor;  $K_m$ , the restoring force (spring constant); and  $\vec{F}$ , the external force applied to the diaphragm. The external force has two components (a and b):

- a. the force resulting from sound pressure  $p_m A_m$ , where  $p_m$  is the average pressure over the diaphragm, and  $A_m$  is surface area of the diaphragm; and
- b. the force resulting from the microphone's bias voltage.

The force resulting from the bias voltage causes the equilibrium position of the diaphragm to shift a small amount ( $x_0$ ), which is given by:

$$x_0/d = C_m V_B^2 / d^2 K_m \quad (52)$$

where  $d$  is the distance between the diaphragm and the back plate of the microphone capacitor when the microphone is unbiased;  $C_m$  is the unbiased microphone capacitance given by:

$$C_m = \epsilon_0 A_m / d \quad (53)$$

and  $V_B$  is the microphone bias voltage.

The restoring force ( $K_m$ ) is produced by the tension ( $T_m$ ) in the microphone diaphragm:

$$K_m = 8\pi T_m \quad (54)$$

This tension must be sufficient to prevent the bias voltage from pulling the diaphragm into contact with the back plate.

The simplest and most common way to bias the condenser microphone is to apply a fixed voltage bias through a large resistor ( $R_B$ ), so that  $(R_B C_m)^{-1}$  is much less than the signal frequencies of interest. The output voltage of the microphone ( $V_s$ ) is given by:

$$V_s = p_m \frac{V_B A_m}{dK_m} \left[ 1 - \left( \frac{\omega^2}{\omega_m^2} \right) - i \left( \frac{\omega}{\omega_m Q_m} \right) \right]^{-1} \quad (55)$$

where  $\omega_m$  is the microphone resonant frequency [ $\omega_m \equiv (K_m/m)^{1/2}$ ], and  $Q_m$  is the quality factor [ $Q_m \equiv (mK_m/\delta)^{1/2}$ ]. The open-circuit voltage sensitivity ( $S_m$ ) is defined as the low-frequency ( $\omega \ll \omega_m$ ) ratio of the signal voltage ( $V_s$ ) to the sound pressure ( $p_m$ ):

$$S_m = V_B A_m / dK_m \quad (56)$$

$S_m$  in terms of the microphone equivalent volume ( $V_m$ ) is found by combining Equations 54, 55, and 56:

$$S_m = V_B V_m / dY P_0 A_m \quad (57)$$

The electrical signal generated by the microphone as a result of the opto-acoustic pressure signal can be calculated from Equation 55 by substituting the proper value for  $p_m$ . In solving Equation 13 to find  $p_m$ , one must consider the effect of the microphone on the acoustic behavior of the gas inside its container (173, 180, 256, 313, 314). The addition of the microphone to the container affects the acoustic modes of the container by changing the boundary conditions on  $p_j$ . In the absence of the microphone, the boundary conditions on the rigid container walls require that the gradient of  $p$  normal to the wall must vanish at the wall. When the microphone is added to the container, the diaphragm forms a part of the container wall and this part is no longer rigid. In this case, the boundary conditions require the acoustic velocity normal to the diaphragm surface to be equal to the diaphragm velocity ( $dx/dt$ ) produced by the acoustic pressure ( $p_m$ ), thus yielding:

$$\left[ \frac{(\nabla p)_N}{p} \right]_m = \frac{A_m}{K_m} \frac{\omega^2 p_0}{[1 - (\omega/\omega_m)^2 - i(\omega/\omega_m Q_m)]} \quad (58)$$

and  $h$  is the boundary condition at the microphone. In Equation 57,  $\langle \phi_0 \rangle_{\text{in}}$  is the quotient of  $p$  normal to the diaphragm. When the microphone is added to the gas container, and Equation 58 is used to describe the boundary condition on  $h$ , the solutions of Equation 18 will not, in general, be orthogonal, and Equations 56, 57, and 58 will not be valid. As a result, solving Equation 17 for the optoacoustic pressure becomes more complex. However, in the case for a microphone coupled to a small sample cell, a simplification can be made to reduce the complexity of this calculation.

If the container is small enough, and the modulation frequency is much less than the respective resonant frequency of the sample cell and microphone, the pressure will be constant and independent of position in the container, and the microphone will behave like an additional volume ( $V_m$ ) added to the sample cell (173, 180, 256, 313, 314). Thus,  $A_0(\omega)$  and  $V_s$  become:

$$A_0(\omega) = \frac{i\alpha(\gamma - 1)W\omega}{\omega(1+i\omega/\tau_T)(V_C + V_m)} \quad (59)$$

$$V_s = \frac{i(\lambda - 1)}{\pi r^2 P_0 A_m} \left( \frac{V_B}{d} \right) \left[ \frac{V_m}{V_C + V_m} \right] (\alpha W\omega) \quad (60)$$

which gives the electrical signal produced by the microphone. These two equations describe the signal generated by an optoacoustic detector. They provide a means of evaluating the effect of design changes on signal amplitude and signal-to-noise performance.

If the dimensions of the sample cell are kept small, the first acoustic resonance mode of the combined microphone and container will occur at the modified resonant frequency of the microphone. The modified spring constant ( $K_m'$ ) can be calculated from the modified effective volume ( $V_m'$ ):

$$(V_m')^{-1} = V_m^{-1} + V_C^{-1} \quad (61)$$

$$K_m' = K_m^{-1} + V_m/V_C \quad (62)$$

The resonant frequency becomes:

$$\omega_1 = \omega_m (1 + V_m/V_C)^{1/2} \quad (63)$$

Assuming that loss comes only from microphone damping, the noise voltage  $\{ |V_{sn}(\omega)|^2 \}$  is calculated by combining Equations 46, 55, and 61-63 (where  $P_0 C^2 = \gamma P_0$ ):

$$|V_{sn}(\omega)|^2 = \left( \frac{4kT_p P_0 C'}{\omega_m Q_m V_m (1 + V_m/V_C)^2} \right) S_m^2 \quad (64)$$

An optoacoustic condenser microphone can also be modelled as a two-terminal electrical network (173, 180, 256, 327-329, 348, 386). The small signal electrical impedance of a biased microphone is identical to a series resistance-inductance-capacitance; and (RLC) resonant circuit shunted by a capacitor. An equivalent circuit is shown in Figure 2, in which  $C_m$  is the microphone high-frequency capacitance, and  $C'$ ,  $L$ , and  $R$  are determined by the restoring force, mass, and damping of the diaphragm, respectively:

$$C' = C_m^2 V_B^2 / d^2 K_m \quad (65)$$

$$L = m/K_m C' = (\omega_m' C')^{-1} \quad (66)$$

$$R = \delta/K_m C' = (Q_m \omega_m C')^{-1} \quad (67)$$

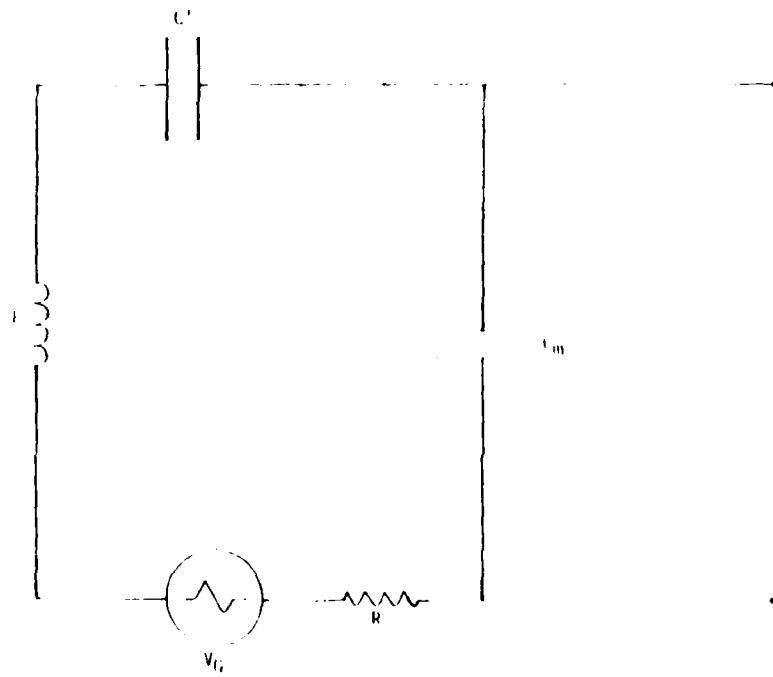


Figure 2. Condenser microphone equivalent electrical circuit.

The signal caused by an acoustic pressure ( $p_m$ ) on the diaphragm appears as a voltage ( $V_G$ ) in series with the RLC' resonant circuit, and is given by:

$$V_G = (A_m d / V_B C_m) p = (C_m / C') S_m p \quad (68)$$

where

$$C_m = \epsilon_0 A_m / d$$

In the mechanical model of the microphone, the noise appeared to be caused by viscosity and heat conduction, which resulted in a finite  $Q$ . In the electrical model, the noise is represented by the resistor Johnson noise. Johnson noise produced by the resistor in the equivalent circuit appears as a noise voltage on the output terminals, and has exactly the same amplitude as the thermal fluctuation noise. The noise at the output terminals of the microphone generated by the Johnson noise in resistor  $R$  is (40, 120, 147, 165, 197, 230, 231, 239, 242, 256, 288, 314):

$$|V_n|^2 = \frac{4kTR}{\omega^2 C_m^2} \left\{ R^2 + \left( \omega L - \frac{1 + V_m/V_C}{\omega C'} \right)^2 \right\}^{-1} \quad (69)$$

In the low-frequency limit, Equation 69 simplifies to:

$$|V_n|^2 = \frac{4kT\rho C'}{\omega_m^2 V_m (1 + V_m/V_C)^2} |S_m|^2 \quad (70)$$

which is identical to Equation 64.

In addition to the thermal fluctuation noise, a significant source of noise will be the microphone preamplifier (Fig. 1). Development of the theory of noise introduced by the microphone-preamplifier combination has been studied by various investigators (7, 24, 29, 78, 80, 102, 173, 174, 179, 180, 197, 229-231, 239, 256, 314, 327-329, 386). A summary of this theory follows.

The microphone electrical equivalent circuit (Fig. 2) is also useful in the development of the preamplifier noise. A model of the microphone and preamplifier equivalent circuit is shown in Figure 3. Preamplifier noise is represented by a series voltage noise source  $\{|V_{na}|^2\}$ , and a shunt current noise source  $\{|I_{nd}|^2\}$ . Noise is also generated by the Johnson noise of the bias resistor ( $R_B$ ); capacitor  $C_2$  and the associated feedback circuit are used to increase the input impedance, and thus increase the low-frequency response. Combining

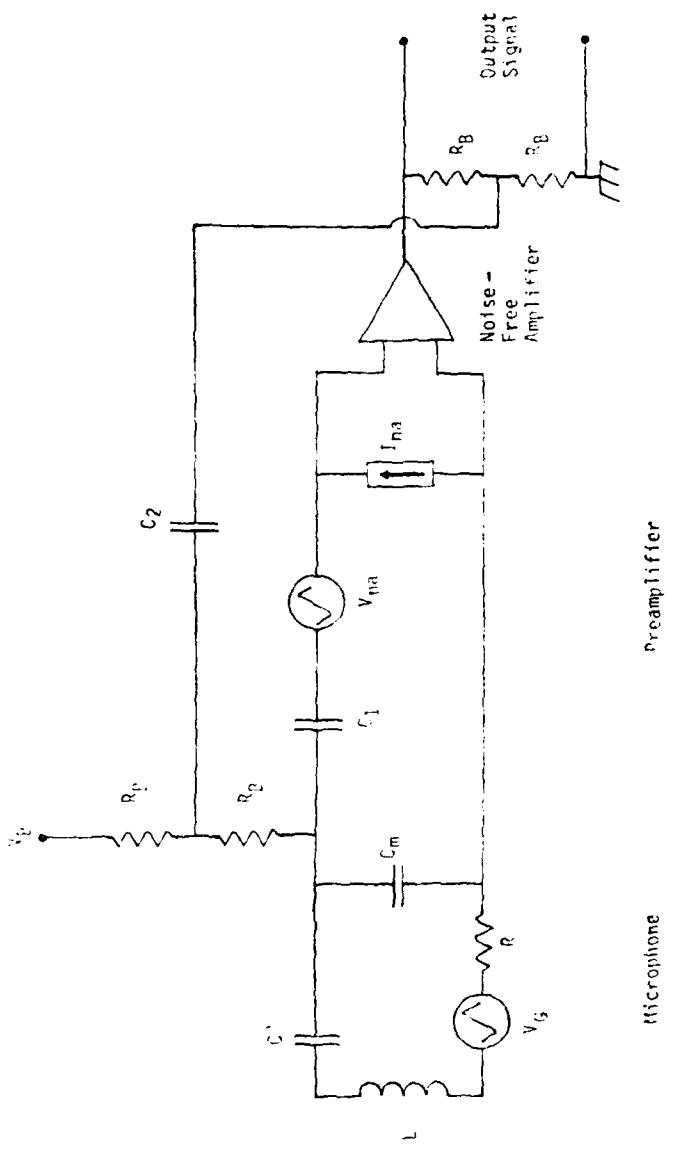


Figure 3. Condenser microphone and preamplifier equivalent electrical circuit noise model.

These three noise sources with the microphone noise yield the power spectrum  $\{V_n\}^2$  of the total noise referred to the preamplifier input:

$$\{V_n\}^2 \approx \{V_{na}\}^2 + \frac{\{I_{nd}\}^2 + 4kT/R_B}{\omega^2 C_m^2} + \frac{4KTC^4}{Q_m \omega^2 C_m^2 (1 + V_m/V_C)^2} \left[ \left( \omega^2/\omega_1^2 - 1 \right)^2 + \left( \omega/\omega_1 Q_1 \right)^2 \right]^{-1} \quad (71)$$

(7, 24, 29, 78, 80, 102, 173, 174, 179, 180, 197, 229-231, 239, 256, 314, 327-329, 386).

#### OPTIMUM DESIGN OF AN OPTOACOUSTIC SPECTROMETER TO DETECT HYDRAZINE FUELS

In designing an optoacoustic spectrometer, the optimum design will depend on the purpose of the system. The ultimate sensitivity of the system for detecting minute amounts of an absorber gas will be determined predominantly by the following six factors:

- a. the smallest absorbed power detectable by the microphone-preamplifier system,
- b. the power density of the irradiating laser beam,
- c. the signal caused by scattering and subsequent absorption of the incident laser beam by the microphone,
- d. the absorption cross section of the molecule to be detected, and
- e. the signal caused by unwanted absorption by other gas constituents (present in the environment) from which a sample is drawn for analysis.

Factors d and e are influenced by judicious selection of the absorption frequencies. This selection process requires a quantity of data about absorption spectra, laser frequencies, and possible interfering gases. The first three factors (a-c) can be optimized by employing several of the equations already developed in the previous section of this report ("Acoustic Signal Detection"). The following paragraphs present an outline that can be used for designing an optoacoustic gas spectrometer for a specific purpose.

Assume that the laser source has a fixed beam power of  $W$  watts, and that the sample cell is small enough and the modulation frequency low enough that the approximations made to derive Equations 60 and 64 are valid. The ultimate system design goal is to achieve the greatest possible absorption sensitivity (maximize the signal-to-noise ratio). The laser modulation frequency ( $\omega$ ), the dimensions of the sample cell, and the microphone design are the parameters that can readily be adjusted.

For simplicity, assume initially that the microphone preamplifier noise is insignificant compared to the combined noise of the entire system. Thus, the signal-to-noise ratio can be calculated from Equations 60 and 64 to yield:

$$\left(\frac{\text{signal}}{\text{noise}}\right)^2 = \frac{(\gamma - 1)^2}{4kT\omega^2} \left(\frac{\ell A_m}{V_C}\right)^2 \left(\frac{\omega_m Q_m}{K_m}\right) \frac{\alpha' W^2}{\Delta f} \quad (72)$$

The factor  $(\gamma - 1)^2$  can be increased in some situations by selecting a monatomic gas such as helium or argon, rather than nitrogen or air, to dilute the sample to be measured. However, in the case where the hydrazine fuels are diluted in air,  $\gamma$  is not adjustable. The factor  $kT$  in the denominator suggests operating the system at as low a temperature as possible. Unfortunately, condensation may prevent lowering  $T$  very much.

The factor  $(\ell A_m/V_C)^2$  can be regarded as a coupling coefficient between the microphone and the sample cell. This factor becomes large when a large area microphone and a small cross-section cell are used. For example, if the sample cell is a cylinder having length  $\ell$  and a cross-sectional area  $A_C$ , the volume is  $V_C = \ell A_C$  and the factor  $(\ell A_m/V_C)^2$  equals  $(A_m/A_C)^2$ . To maximize this factor, the smallest possible cross-sectional area is selected. This area, however, is influenced by the requirement to focus the laser beam into the container. For example, if the laser beam is of wavelength  $\lambda$  and operating in the lowest order transverse mode, then the minimum beam diameter at the ends of the gas container is achieved when the beam confocal parameter equals the cell length (79). The resultant beam radius ( $w$ ) at the input and output windows is:

$$w = (\lambda \ell / \pi)^{1/2} \quad (73)$$

The beam radius ( $w$ ) is the distance from the center of the beam at which the electric field strength is  $e^{-1}$  of its value at the beam center. The intensity at this point is  $e^{-2}$  of its value at the beam center. Selecting ( $w$ ) as the radius of the cylindrical sample cell allows most of the available laser beam power to enter the cell. The cell area becomes:

$$A_C = \lambda \ell \quad (74)$$

Substituting these results into Equation 72 yields:

$$\left(\frac{\text{signal}}{\text{noise}}\right)^2 = \frac{(\gamma - 1)^2}{4kT\omega^2} \left(\frac{A_m}{\lambda \ell}\right)^2 \frac{\alpha' W^2}{\delta(\Delta f)} \quad (75)$$

This equation indicates that the signal-to-noise ratio increases as the frequency is reduced. Equation 75 was derived from the assumption that  $\omega \gg \tau_f^{-1}$ . Thus, one must evaluate Equation 59 to understand the low-frequency dependence of the signal-to-noise ratio. Equation 59 indicates that the signal-to-noise ratio is maximum when the frequency is very low. Practical considerations, such as  $\tau_f^{-1}$  noise in electronics, make it more realistic to select  $\omega \approx \tau_f^{-1}$ . This choice will reduce the signal-to-noise ratio by a factor of  $\sqrt{2}$  from its ideal low-frequency limit.

The preamplifier noise was neglected in the foregoing analysis. When preamplifier noise is present, optimum system design will depend on the nature of the preamplifier noise. The signal amplitude below resonance (Eq. 60) indicates the signal amplitude can be increased by selecting a large microphone equivalent volume. The maximum signal amplitude is achieved for  $V_m \gg V_C$ . A design goal of  $V_m \approx V_C$  can readily be achieved. At low frequencies, the preamplifier current and Johnson noise from the bias resistor are the main noise sources. If the combined noise from these two noise sources is larger than the microphone fluctuation noise, the signal-to-noise ratio is independent of frequency. If the preamplifier voltage noise is sufficiently small, this frequency independence will be maintained up to the resonant frequency ( $\omega_1$ ). At this resonance, the signal-to-noise ratio is enhanced by a factor of  $Q$ . Thus, operating at resonance is desirable if the preamplifier voltage noise is small and the dominant noise source is amplifier current noise. When this source is fluctuation noise, the signal and noise are increased equally by resonance, and the optimum operating condition remains  $\omega_f \approx \tau_f^{-1}$ . Under the condition where several noise sources contribute, or  $|V_{na}|^2$  and  $|I_{na}|^2$  are not independent of frequency, the optimum operating frequency may be different from  $\tau_f^{-1}$  or  $\omega_1$  (173, 174, 180, 256).

The purpose of the following paragraphs is to utilize the absorption spectra data on the hydrazine fuels, manufacturers' equipment specifications, and the significant equations developed in this report to specify an optoacoustic spectrometer design to detect the hydrazine fuels.

#### Laser Wavelength Selection

The most convenient radiation to use in an optoacoustic system is the infrared (IR). This radiation is absorbed by many pollutants of interest at wavelengths emitted by commercially available IR lasers, and the absorption dependence on wavelength is characteristic of the molecular structure of the gas. Fortunately the bulk of air ( $N_2, O_2$ , etc.) is almost transparent to IR radiation (6, 28, 48, 52, 70, 81, 92, 107, 110, 115, 124, 152, 176, 188, 205, 263, 271, 277, 317, 318, 322, 330, 351, 356, 368, 369, 383).

The IR absorption spectra of the hydrazine fuels (hydrazine, MMH, UDME) appear in Figures 4-6. Considering the commercially available isotopic CO<sub>2</sub> lasers, the hydrazine fuel absorption spectra, and the absorption spectra of the common atmospheric constituents that could be interferences, an operating wavelength range of 10.7 to 10.9  $\mu\text{m}$  appears optimum (2, 28, 48, 59, 70, 81, 110, 124, 152, 176, 188, 221, 222, 271, 317, 318, 322-326, 351, 368, 383). The Sylvanian Model 950A sealed-tube, isotopic CO<sub>2</sub> ( $^{13}C/^{12}C$ ), 5-watt laser satisfies these requirements. The technical specifications for the laser are listed in Table 2; the tunable operating wavelengths, in Table 3; and the dimensional specifications, in Figure 7 (324-325).

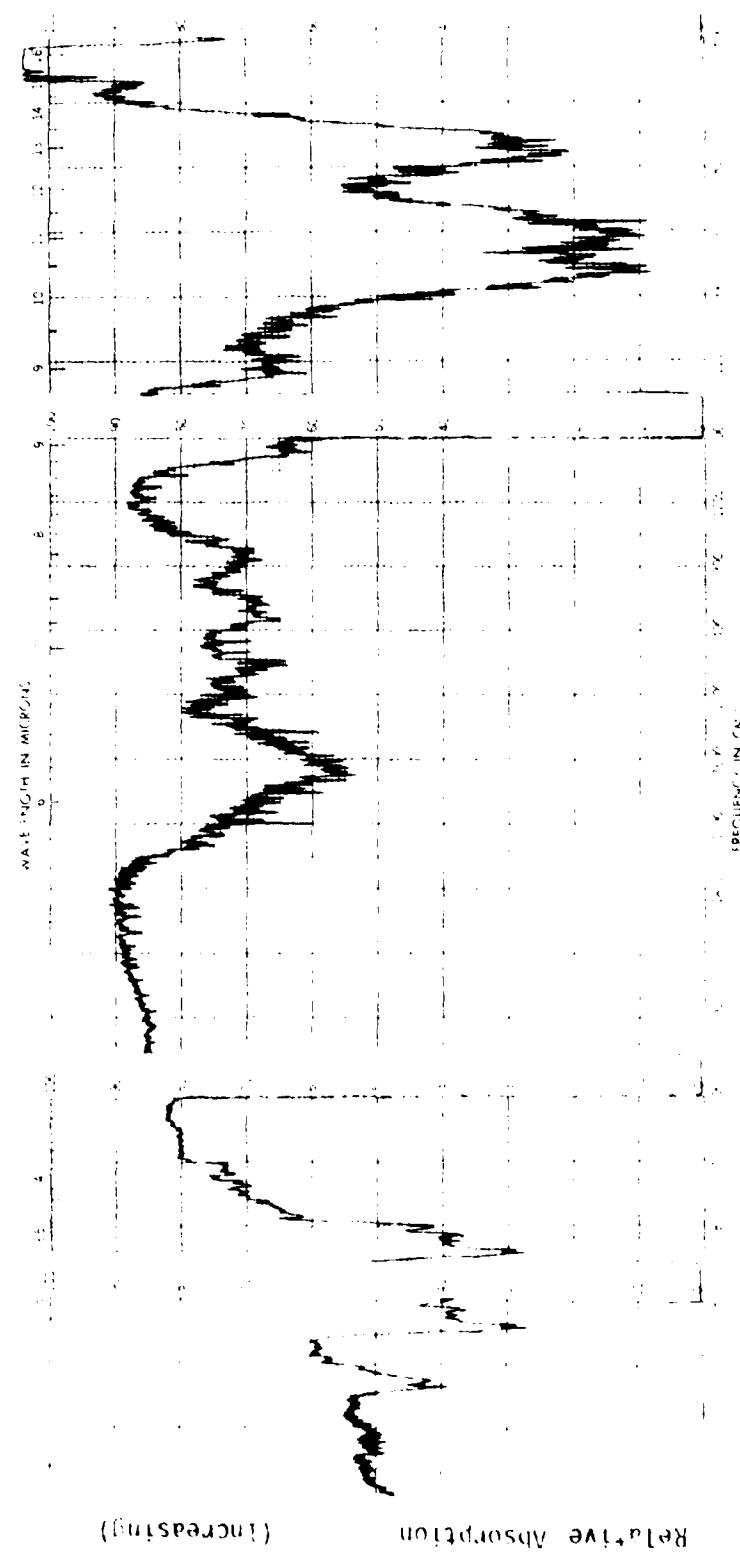


Figure 4. Hydrazine absorption spectra.

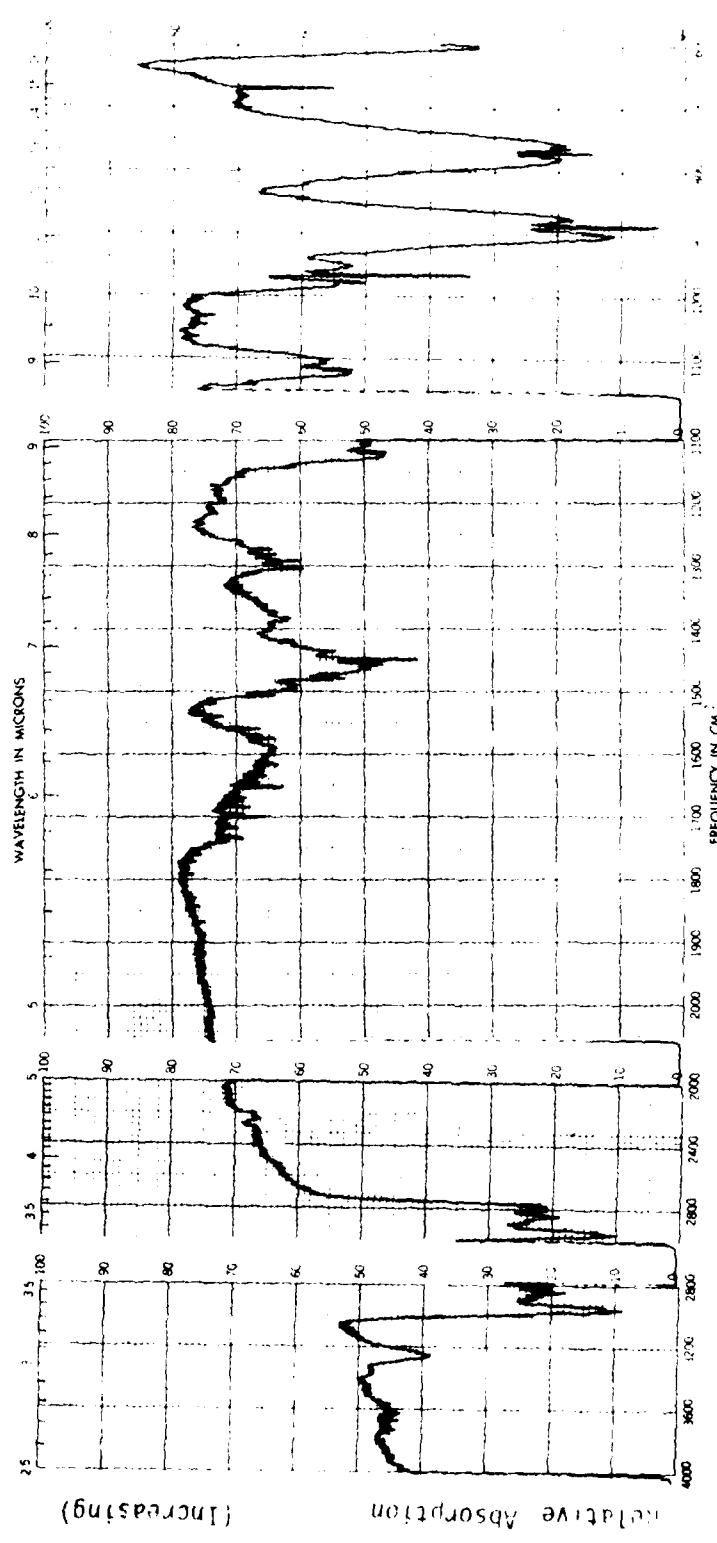


Figure 5. Monomethylhydrazine (MMH) absorption spectra.

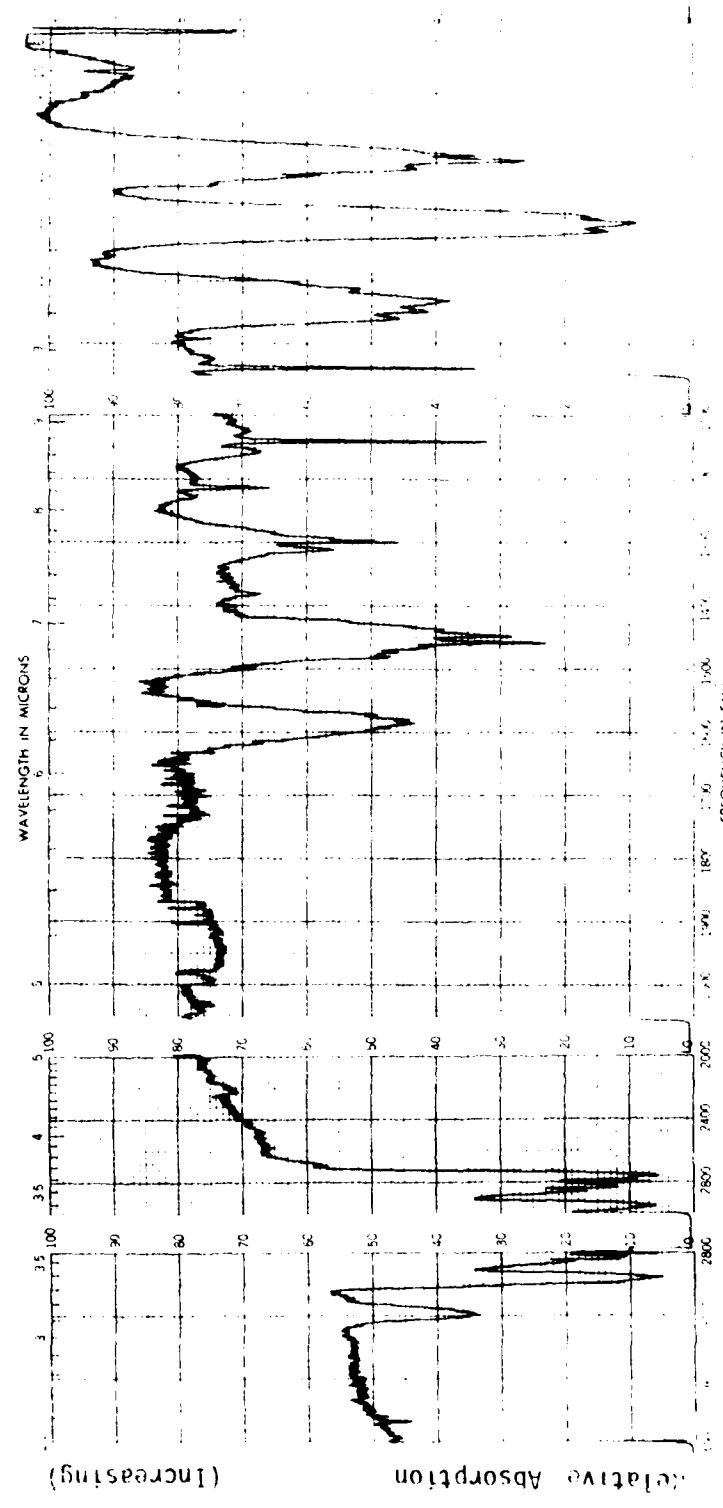


Figure 6. Absorption spectra of 1,1-dimethylhydrazine (UDMH).

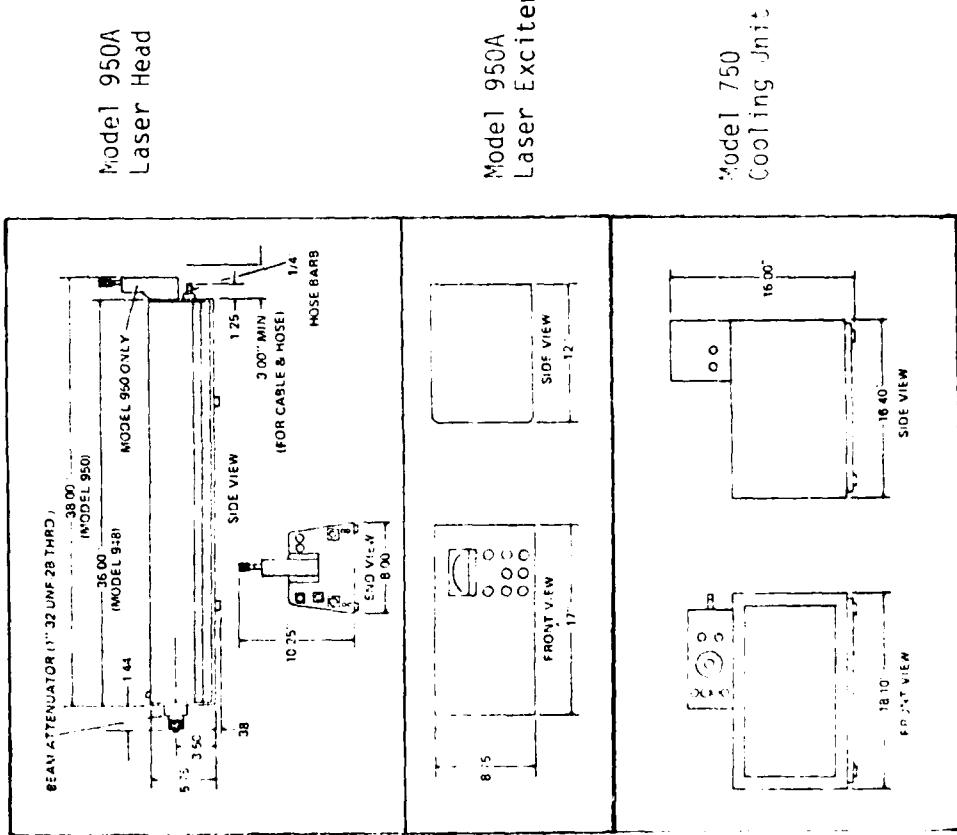


Figure 1. Dimensional specifications for the Sylvania model 950A laser head, laser exciter, and model 750 cooling unit.

TABLE 2. TECHNICAL CHARACTERISTICS OF SYLVANIA MODEL  
950A CO<sub>2</sub> LASER

<u>Property</u>	<u>Value</u>
Output Wavelength (μm)	Tunable over 20 wavelengths 10.71 - 10.812 μm
Power Output	5 watts minimum at 10 or more wavelengths
Mode Purity	11 Mode
Beam Diameter (e=1 field points)	5 mm
Beam Divergence (full angle)	<3.5 mrad
Polarization (E-vector)	Vertical
Amplitude Stability	5% long-term 0.5% short-term
Frequency Stability (Long-Term: Hours)	<50 MHz (1:106); <5 MHz with Auxiliary Model 750 cooling unit
Frequency Stability (short-term: 0.1 sec)	<50 kHz (2:109)
Wavelength Selection	Calibrated In-Cavity Diffraction Grating
Optical Cavity length	77 cm
Cooling Requirements	1-4 GPM
Power Requirements	115 volts, 50/60 Hz, 600 watts
Optical Cavity Mirrors	Total Reflecting Grating 3-meter Radius of Curvature
High Voltage Source Location	Laser Head
Hardware Included	Piezoelectric Stack and Power Source, Calibrated Grating, Current Meter, Flow Switch, Interlocks, Laser Head, and Power Supply
Size: Laser Head (in.) Power Supply (in.)	6 x 8 x 38 5-1/4 x 14 x 17
Weight: Laser Head (lb) Power Supply (lb)	35 46
Warranty	1 year, including tube
Cost (Dec 79)	\$16,460
Cooling Unit	Model 750
Cooling Unit Cost (Dec 79)	\$ 1,725

TABLE 3. SYLVANIA MODEL 950A TUNABLE LASER WAVELENGTHS  
 (00°1 - 10°0) BAND

<u>Transition</u>	<u>Wavelength (<math>\mu m</math>)</u>	<u>Output (W)</u>
P8	10.476	3.6
P10	10.495	5.8
P12	10.514	6.9
P14	10.533	6.9
P16	10.552	7.3
P18	10.571	7.6
P20	10.591	7.8
P22	10.612	7.7
P24	10.632	7.5
P26	10.653	7.5
P28	10.675	7.0
P30	10.697	6.4
P32	10.719	6.5
P34	10.742	5.7
P36	10.765	4.7
P38	10.788	4.3
P40	10.812	3.1
P42	10.836	2.1
R6	10.350	1.2
R8	10.333	5.4
R10	10.319	6.7
R12	10.304	7.5
R14	10.289	7.3
R16	10.275	8.1
R18	10.261	8.3
R20	10.247	8.4
R22	10.234	8.5
R24	10.220	8.3
R26	10.208	8.0
R28	10.195	7.5
R30	10.182	6.8
R32	10.171	5.8
R34	10.159	4.3

### Variable-Speed Chopper

In order to use a continuous wave (CW) laser in an optoacoustic spectrometer, the light entering the sample must be modulated. The light energy can be frequency or amplitude modulated. The preferable method is to amplitude modulate (chop) the laser light. Motor-driven slotted-wheel mechanical choppers have been designed for this purpose (87-89, 105, 108, 142, 189, 190, 278, 289). For this type of system, the actual chopping rate is determined by multiplying the number of apertures or slots in the rotating wheel by the rotational speed of the drive motor. To minimize the synchronous background signal caused by a motor-driven chopper wheel, the wheel must be balanced and vibrationally decoupled from the sample cell by means of shock-absorbing mounts. In addition, the chopper and sample cell should be spaced as far apart as possible; this step usually involves placing the chopper wheel near the laser exit window. Also desirable is minimizing the rotational velocity of the wheel by using a maximum number of apertures. McClelland and Kniseley have suggested the use of a solid chopper wheel (no slots) to reduce acoustic emission (206-208). Such a wheel could, for example, be made by depositing or photo-etching a metallic film pattern onto a fused silica disc.

Oscillatory devices, such as a tuning-fork chopper or a galvanometer-driven mirror-vane, can also be used for modulating the laser energy. However, such devices are usually limited in frequency and/or aperture.

Mechanical chopping can be avoided altogether if a pulsed laser is used. A brief investigation of this approach, however, revealed no commercial source with an acceptable combination of pulse energy and lifetime.

The mechanical variable-speed light-chopper suitable for this task is the Princeton Applied Research Model 192 Variable Speed Light Chopper. This unit has a variable chopping rate ranging from 5 to 5500 cycles/sec (Hz) (190, 278). Integrated circuitry provides dual reference signals (0 - 5 volt peak square waves) at chopping rates suitable for synchronizing the reference channels of the lock-in amplifiers that will be used in this optoacoustic spectrometer design. A brushless direct-current drive motor eliminates electrical noise caused by commutator arcing, and minimizes increases in operating temperature. Maximum temperature rise for this type of motor in continuous operation is less than 10°C, a characteristic especially important in IR work where warmer chopping blades act as an extraneous noise source. A shock-mounting plate provides mechanical isolation between the chopper motor assembly and the work surface.

### Microphone and Preamplifier

The pressure oscillation amplitudes in a sample cell can be detected with various transducers, including condenser, electret, and piezoelectric microphones (7, 20, 29, 34, 35, 39, 54, 55, 68, 71, 78, 80, 81, 96-98, 102, 114, 118, 143, 150, 152, 160, 173, 174, 179, 180, 198, 203, 204, 208, 212, 218, 219, 230, 231, 240, 256, 257, 264, 280, 287, 309, 313, 327-329, 339, 348). The condenser microphone is the most sensitive and possesses a flat frequency response in the modulation frequency range of interest for optoacoustic spectroscopy.

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The most sensitive microphone-preamplifier combination identified from commercial sources is the Brüel & Kjaer Model 4144 air condenser microphone and Model 2619 low-noise preamplifier (63, 109, 214, 218, 219, 339). The important technical characteristics of the microphone and preamplifier are summarized in Tables 4 and 5, respectively (63, 109, 214, 218, 219, 339).

#### Laser Power Meter

A laser power meter is employed as a reference detector in the optoacoustic spectrometer shown in Figure 1. The use of this meter permits the optoacoustic signal to be normalized; and, as a result, temporal effects of laser power variations are eliminated (290). The instrument most suitable for this application is a thermopile detector (Model 210), manufactured by Coherent Radiation (184). The technical specifications for this power meter are summarized in Table 6 (184).

#### Lock-In Amplifier

The lock-in amplifier is one of the most common and effective instruments designed to measure extremely weak signal intensities in the presence of noise (1, 2, 24, 41, 44, 46, 62, 63, 66, 67, 74, 80, 90, 93, 99, 120, 131, 172, 190, 225, 230, 231, 243, 244, 278, 286, 302, 314, 337, 349, 350, 364, 385). In principle, they operate as extremely narrow-band detectors. A measurement in which a lock-in amplifier is utilized involves three main operations: amplitude modulation (AM) of a carrier wave with the desired signal information; selective amplification; and synchronous AM demodulation. The AM step is implemented at some specific point in the experimental system (e.g., chopping of laser light); and the lock-in amplifier performs the last two processing steps (1, 24, 41, 44, 46, 62, 63, 66, 74, 90, 93, 99, 120, 131, 225, 243, 244, 337, 349, 350).

The key step in a lock-in amplifier measurement (the step which gives the technique its name) is synchronous AM demodulation. Synchronous demodulation involves multiplication of the modulated carrier wave by a reference signal (chopper reference signal) which has exactly the same frequency as the carrier wave and is phase-locked to the carrier wave at zero degrees phase shift. Demodulation is completed by integrating the output of the multiplication step; this process can be accomplished using a low-pass filter.

A block diagram of a conventional lock-in amplifier is shown in Figure 8. Two input channels are provided: one to process the signal to be measured (amplitude modulated carrier); and one to process the reference signal. In almost all lock-in amplifier optoacoustic spectroscopy systems, the phase-lock reference signal is implemented by chopping the light beam with a mechanical chopper. The reference signal is then phase-locked to the carrier frequency, but is not, in general, locked at a zero degrees phase differential. Thus, a phase shifter is required in order that the relative phase of the reference signal can be adjusted with respect to the carrier signal. The comparator in the reference channel converts the reference to a bipolar square wave before this waveform is applied to the four-quadrant multiplier. Selective or tuned amplifiers are also included in each channel, and are used to exclude broad-band and discrete noise at the desired signal frequencies. The four-quadrant multiplier generates a

TABLE 4. DESIGN AND OPERATING CHARACTERISTICS OF CARTRIDGE MICROPHONE MODEL 4144  
AIRCRAFT GRADE MICROPHONE

Property	Value
Frequency response characteristic	Pressure
Open circuit frequency Response, flat within $\pm 2$ db ( $\Delta \pm 2.5$ db)	2.6 Hz to 8 kHz
Nominal Diameter	1 in.
Open circuit distortion limit (3%) dB re 20 $\mu$ Pa	>148
Temperature Coefficients between $-50^{\circ}\text{C}$ and $+60^{\circ}\text{C}$ (db/ $^{\circ}\text{C}$ )	0.008
Expected long-term stability (extrapolated)	(at $25^{\circ}\text{C}$ ) >900 years/db (at $150^{\circ}\text{C}$ ) 1.2 hour/db
Influence of static Pressure (db/atm)	-2
Influence of vibration (1 g in axial direction) db re 20 $\mu$ Pa	±8
Influence of Relative humidity	<0.1 db
Height of cartridge: without protecting grid; with protecting grid	17 mm 19 mm
Diameter of Cartridge: without protecting grid; with protecting grid	23.77 mm 23.77 mm
Thread for protection grid or coupler mounting	25.17 mm - 6T NS2
Thread for preamplifier mounting	25.11 mm - 5.5 TNS2
Diaphragm Mass (kg)	$1.4 \times 10^{-5}$
Diaphragm Spring Constant (N-m $^{-1}$ )	$5.83 \times 10^{14}$
Diaphragm damping N - sec - m $^{-2}$	$9.24 \times 10^{-1}$
Microphone Equivalent Volume (cm $^3$ )	0.15
Open Circuit Sensitivity (V-N $^{-1}$ -m $^{-2}$ )	$5 \times 10^{-2}$
High-frequency Capacitance (F)	$44 \times 10^{-11}$
Mechanical Quality Factor	0.8
Bias Voltage (V)	200
Distance Between Diaphragm and Back Plate of Condenser (m)	$2 \times 10^{-5}$
Microphone Diaphragm Area (m $^2$ )	$1.92 \times 10^{-4}$
Microphone Resonant Frequency (Hz)	$8.34 \times 10^4$

TABLE 5. TECHNICAL CHARACTERISTICS OF BRJELL & KJAER MODEL 2019  
PREAMPLIFIER AND MODEL 2804 POWER SUPPLY

<u>Property</u>	<u>Value</u>	
Power Supply	120V/2 mA	28V/0.5 mA
	Heater 6V/60 mA	
Polarization Voltage	Transmitted through preamplifier to microphone cartridge from power supply	
Input Impedance	>10 $\Omega$ // 0.8 pF	>70M // 1 pF
Output Impedance	<25 $\Omega$	<70 $\Omega$
Maximum Output Current	1.5 mA peak	0.5 mA peak
Pulse Rise Time	0.2 $\mu$ s	0.2 $\mu$ s
Pulse Decay Time	0.6 $\mu$ s	0.6 $\mu$ s
Temperature Range	-20° to + 60°C (-4° to + 140°F)	-20° to + 60°C (-4° to + 140°F)
Attenuation (Preamplifier alone)	<0.03 dB	<0.1 dB
Preamplifier Noise (dummy microphone) (Lin. 20 Hz to 200 kHz and A-weighted)		
60 pF (1 in. microphone)	<15 $\mu$ V	<2.5 $\mu$ V
17 pF (1/2 in. microphone)	<25 $\mu$ V	<4.5 $\mu$ V
6 pF (1/4 in. microphone)	<50 $\mu$ V	<15 $\mu$ V
3.5 pF (1/8 in. microphone)	<70 $\mu$ V	<25 $\mu$ V
Dimensions: Diameter:	12.7 mm (0.5 in.)	
Length:	83 mm (3.25 in.)	
Cable Length	2 m (6.6 ft)	

TABLE 6. TECHNICAL CHARACTERISTICS OF COHERENT RADIATION  
MODEL 210 LASER POWER METER

<u>Property</u>	<u>Value</u>
Detector	Thermopile
Spectral Range ( $\mu$ m)	0.3 - 30
Maximum Power Capacity (watts)	10
Rise Time ( $\mu$ sec)	1
Accuracy (per cent)	5
Active Detector Area ( $\text{mm}^2$ )	1.81
Price (Dec 79)	\$1,200

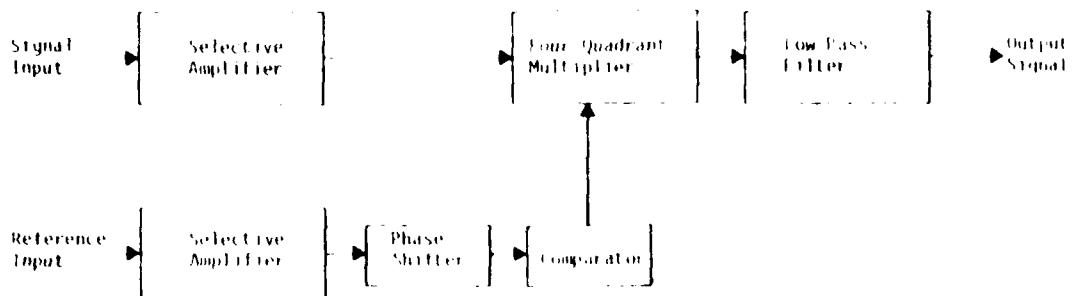


Figure 8. Conventional lock-in amplifier block diagram.

product of the phase-compensated carrier and reference signals. This multiplication process produces the desired information in a band of frequencies about the zero frequency component. Demodulation of the desired signal is completed by integrating the output of the multiplication process using a low-pass filter.

Several commercially available lock-in amplifiers are suitable for processing optoacoustic spectroscopy signals (1, 87, 88, 89, 90, 93, 138, 139, 140, 141, 142, 193, 249, 255, 280, 281, 331, 332, 341, 349, 350). These are, in general, complete processing systems and are very flexible in their application. Most of these systems merely require a direct connection to a suitable transducer (condenser microphone/preamplifier) and reference signal (mechanical chopper). A strip-chart recorder connected to the lock-in amplifier's output is convenient for producing a permanent record of the processed information. The most versatile lock-in amplifier for this optoacoustic spectrometer application is the Princeton Applied Research Corporation (PARC) Model 124A with plug-in preamplifier Model 117 (90, 93, 193, 249, 280, 281, 331, 332, 341, 350). A summary of the technical characteristics for this lock-in amplifier and preamplifier combination appears in Table 7 (90, 93, 193, 249, 280, 281, 331, 332, 341, 350).

#### Ratiometer

Compensation and normalization of laser beam temporal intensity fluctuations and phase changes can be accomplished using the configuration of lock-in amplifiers and ratiometer shown in Figure 1. (The function of the lock-in amplifiers has been discussed in the foregoing section.) Normalization of the two lock-in amplifier output signals can be accomplished with several commercially available instruments (144, 249, 290, 331, 332). The ratiometer most suitable for this optoacoustic spectrometer design is the Princeton Applied Research Corporation (PARC) Model 188 Precision Digital Ratiometer (249, 331, 332). The electrical output characteristics of this ratiometer are compatible with most laboratory strip-chart recorders. A summary of the technical specifications for the Model 188 ratiometer is presented in Table 8 (249, 331, 332).

TABLE 7. TECHNICAL CHARACTERISTICS OF PRINCETON APPLIED RESEARCH CORPORATION MODEL 124A LOCK-IN AMPLIFIER AND MODEL 117 PREAMPLIFIER

<u>Property</u>	<u>Value</u>
Frequency Range (Hz)	$2-210 \times 10^3$
Maximum Full-Scale Sensitivity (nanovolts)	100
Time Constant	1 millisecond - 300 sec (6-12 dB/octave)
Signal Channel: Modes of Filtering and Input Impedance ( $Z_{in}$ )	Modes: Notch, Flat, High-Pass, Low-Pass, and Bandpass. $Q = 1-100$ with 10 per cent Equivalent Noise Bandwidth $Z_{in} = 100$ megohms shunted by 20 picofarad capacitance
Reference Channel Modes	Internal Voltage Controlled Oscillator
Output Stability (> in 24-hour period)	15 ppm
Calibration Level	20 nanovolts to 100 millivolts in 21 levels >>0.5 per cent (1 microvolt to 100 millivolts) 1 per cent (20 nanovolts to 500 nanovolts)
Price (with preamplifier) (Dec 79)	\$4,785

#### Sample Cell Design

In designing an optoacoustic system, the optimum configuration depends on the specific application. The equations presented in the preceding section of this review can be used to design an optoacoustic spectrometer to measure the hydrazine fuels.

This design will use a nonresonant, single-pass sample cell; and the microphone will be coupled directly to the gas container. The microphone and preamplifier technical characteristics appear in Tables 4 and 5 (68, 109, 214, 218, 219, 339). The laser will be operated at a wavelength of 10.812  $\mu\text{m}$ . For simplicity, the sample cell and microphone equivalent volumes are assumed equal ( $V_C = V_M$ ).

Thus the radius and length of an optimally designed nonresonant single-pass cell can be calculated from Equations 73 and 74:

$$l = (V_m/\lambda)^{1/2} = 11.78 \text{ cm} \quad (76)$$

$$w = (V_m/\pi l)^{1/2} = 6.366 \times 10^{-2} \text{ cm} \quad (77)$$

TABLE 2. TECHNICAL CHARACTERISTICS OF PRINCETON APPLIED  
RESEARCH MODEL 188 PRECISION DIGITAL RADIOMETER

<u>Property</u>	<u>Value</u>
Features	<ul style="list-style-type: none"> <li>• 4-1/2 Digit Display</li> <li>• Ratio (A/B)</li> <li>• Log Ratio (log A/B)</li> <li>• Direct Input Display of Channel A or B</li> <li>• Log of Direct Input (log A or B)</li> </ul>
Input Sensitivity	10 volts full scale for Channel A or B
Input Coupling	Direct current coupled
Input Impedance	200 kilohms
Maximum Input Voltage	> 10 volts full scale
Input Offset Voltage	> 5 microvolts per degree Centigrade
Accuracy	> 0.3 per cent average
Outputs	<ul style="list-style-type: none"> <li>• Direct Ratio Output: 10 volts full scale</li> <li>• Log Output: 1 volt per decade</li> <li>• Output Impedance: 1 kilohm</li> <li>• Output offset voltage: 100 microvolts per degree Centigrade</li> </ul>
Cost (Dec 1979)	\$1,740

The thermal damping time ( $\tau_T$ ) can be calculated by equating it to the reciprocal of the frequency at which  $\omega_h$  (given by Eq. 37) is equal to the container radius:

$$\tau_T \approx \rho_0 C_p w^2 / 2k \quad (78)$$

Substituting the values for air at STP [ $\rho_0 = 1.29 \times 10^{-3} \text{ gm} \cdot \text{cm}^{-3}$ ,  $C_p = 0.24 \text{ cal} (\text{gm} \cdot \text{deg})^{-1}$ , and  $k = 5.48 \times 10^{-5} \text{ cal} (\text{cm} \cdot \text{sec} \cdot \text{deg})^{-1}$ ] yields:

$$\tau_T \approx 1.145 \times 10^{-2} \text{ sec} \quad (79)$$

The noise equivalent power (NEP) can be calculated from Equation 47. Since the effective spring constant is doubled when the microphone is coupled to the gas container, it follows that  $\omega_1 Q_1 = 2 \omega_m Q_m$ . The optimum modulation frequency is  $\omega \approx \tau_T^{-1}$ . For the speed of light ( $c = 3.31 \times 10^4 \text{ cm} \cdot \text{sec}^{-1}$ ) and  $\gamma = 1.403$ , Equation 47 yields:

$$\text{NEP} = 3.6 \times 10^{-11} \text{ W}/(\text{Hz})^{1/2} \quad (80)$$

Since the absorbed power is ( $W\omega$ ), the minimum detectable absorption ( $\alpha_{\min}$ ) is:

$$\alpha_{\min} = 3.06 \times 10^{-12} \text{ W}/[\text{cm} \cdot (\text{Hz})^{1/2}] \quad (81)$$

The values of the electrical circuit elements in the equivalent circuit of Figure 2 can be calculated using the data from Tables 4 and 5. Substituting into Equation 65 yields:

$$C_m/C' = 8.7 \quad (82)$$

Therefore,

$$C' = 5.1 \times 10^{-12} \text{ farads} \quad (83)$$

When the microphone is coupled to the sample cell, the spring constant is doubled and the series capacitance ( $C'$ ) for the equivalent circuit is given by

substitution into Equation 68, where  $V_G$  is in volts and  $p_{in}$  is in dynes-per-square centimeter. Thus,

$$V_G = 4.4 \times 10^{-2} p_{in} \quad (84)$$

The values of the inductance ( $L$ ) and resistance ( $R$ ) are given by substitution into Equations 66 and 67. Thus,

$$L = 71 \text{ henries} \quad (85)$$

$$R = 4.68 \times 10^6 \text{ ohms} \quad (86)$$

The Johnson noise voltage generated by this resistor ( $R$ ) is:

$$(4kTR)^{1/2} = 280 \text{ nanovolts}/(\text{Hz})^{1/2} \quad (87)$$

Combining Equations 84 and 87 yields the equivalent noise pressure:

$$\overline{(p_{noise}^2)}^{1/2} = 6 \times 10^{-6} \text{ dyne} \cdot \text{cm}^2/(\text{Hz})^{1/2} \quad (88)$$

If the frequency is well below resonance ( $\omega \ll \omega_1$ ), the voltage given by Equation 88 appears as a voltage at the input terminals of the preamplifier:

$$\overline{(V_{nm}^2)}^{1/2} = 29 \text{ nanovolts}/(\text{Hz})^{1/2} \quad (89)$$

In order for the preamplifier not to be the limiting noise source, the amplifier voltage and current noise must be small compared to this value, that is:

$$(|V_{na}|^2)^{1/2} < 29 \text{ nanovolts}/(\text{Hz})^{1/2} \quad (90)$$

$$(|I_{na}|^2)^{1/2} < \omega C_m (|V_{nm}|^2)^{1/2} = 10^{-16} \text{ amperes}/(\text{Hz})^{1/2} \quad (91)$$

Assuming that the current noise is produced by shot noise in the leakage current of the input field-effect transistor (FET) of the preamplifier, the leakage current,  $I_L$ , is restricted to:

$$I_L < 0.06 \times 10^{-12} \text{ amperes} \quad (92)$$

The results of the foregoing calculations are summarized in Table 9. The sample cell for a hydrazine fuel optoacoustic spectrometer is shown in Figure 9. A schematic of the optoacoustic system shows the integration of all components specified in this analysis (Fig. 10). The relative equipment costs are summarized in Table 10.

#### CONCLUSION

This analysis has presented the basic theory of optoacoustic spectroscopy oriented toward designing a specific system to measure the hydrazine fuels. The fundamental goal in designing this system has been to measure absorption with the greatest possible sensitivity and, thus, maximize the signal-to-noise ratio. In this analysis, all vital components have been selected from commercially available sources and integrated into a system design.

A word of caution is due, however, because only the fundamental sources of noise have been considered. In any real system, additional noise sources may further degrade performance. Some commonly encountered problems are extraneous acoustic noise, vibration-induced noise, and unwanted signals generated by absorption of laser beam energy by sample cell walls and windows. To fine-tune a specific system, each of these practical problems would have to be resolved. For such purposes, experimentation has yielded the best results in the past, and would be expected to do so in the future.

TABLE 9. SUMMARY OF OPTIMUM DESIGN PARAMETERS FOR A HYDRAZINE FUEL  
OPTOACOUSTIC SPECTROMETER

<u>Parameter</u>	<u>Value</u>
Sample Cell Optical Path Length ( $\ell$ )	11.78 cm
Radius of Sample Cell ( $w$ )	$6.366 \times 10^{-2}$ cm
Zero-Order Mode Damping Time ( $\tau$ )	$1.145 \times 10^{-2}$ sec
Noise Equivalent Power (NEP)	$3.6 \times 10^{-11} \text{ W}/(\text{Hz})^{1/2}$
Minimum Detectable Absorption ( $\alpha_{\min}$ )	$3 \times 10^{-12} \text{ W}/[\text{cm} \cdot (\text{Hz})^{1/2}]$
Signal Source Voltage ( $V_G/P_m$ )	$4.4 \times 10^{-2} \text{ V}/(\text{dyne} \cdot \text{cm}^2)$
Microphone Series Resonant Capacitance ( $C_s$ )	$5.1 \times 10^{-12}$ farads
Microphone Series Resonant Inductance ( $L$ )	71 Henries
Microphone Series Resonant Resistance ( $R$ )	$4.68 \times 10^6$ ohms
Equivalent Noise Diaphragm Pressure ( $\bar{P}_n$ ) <sup>1/2</sup>	$6 \times 10^{-6} \text{ dyn}/[\text{cm}^2 \cdot (\text{Hz})^{1/2}]$
Noise Voltage at Preamplifier Input Resulting from Thermal Fluctuation in Microphone and Sample Cell ( $V_{nm}$ ) <sup>1/2</sup>	29 nanovolts/(\text{Hz}) <sup>1/2</sup>
Amplifier Noise Voltage (Upper Limit) ( $\bar{V}_{na}$ ) <sup>1/2</sup>	<29 nanovolts/(\text{Hz}) <sup>1/2</sup>
Amplifier Current Noise (Upper Limit) ( $\bar{I}_{na}$ ) <sup>1/2</sup>	< $10^{-16}$ amperes/(\text{Hz}) <sup>1/2</sup>
FET Gate Leakage Current (Upper Limit) ( $I_g$ )	< $0.06 \times 10^{-12}$ amperes

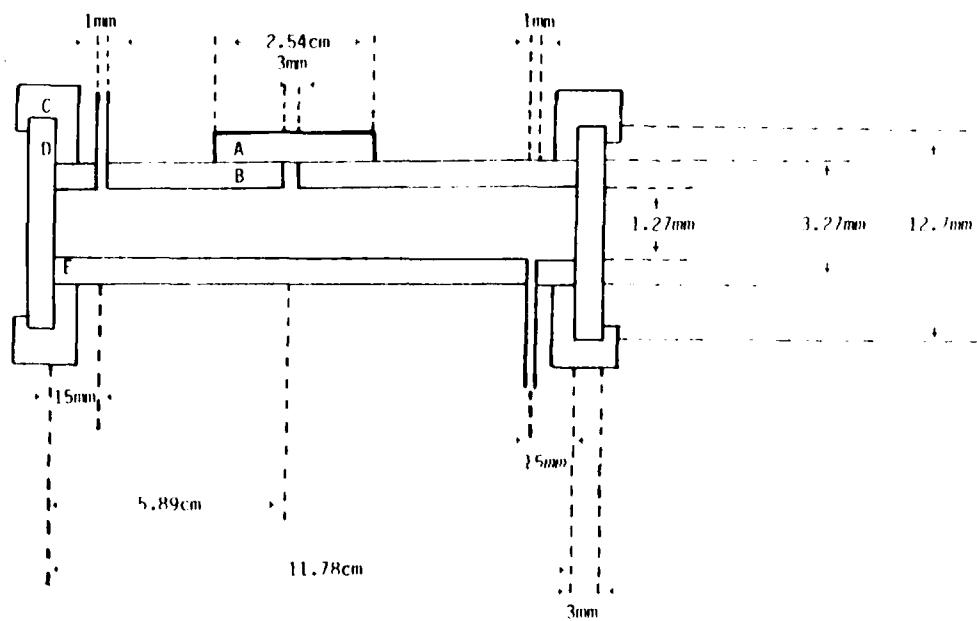


Figure 9. Nonresonant single-pass sample cell design.

[KEY: A = microphone,  
 B = stainless-steel sample cell,  
 C = window collar,  
 D = BaF<sub>2</sub> window, and  
 E = "O" ring seal]

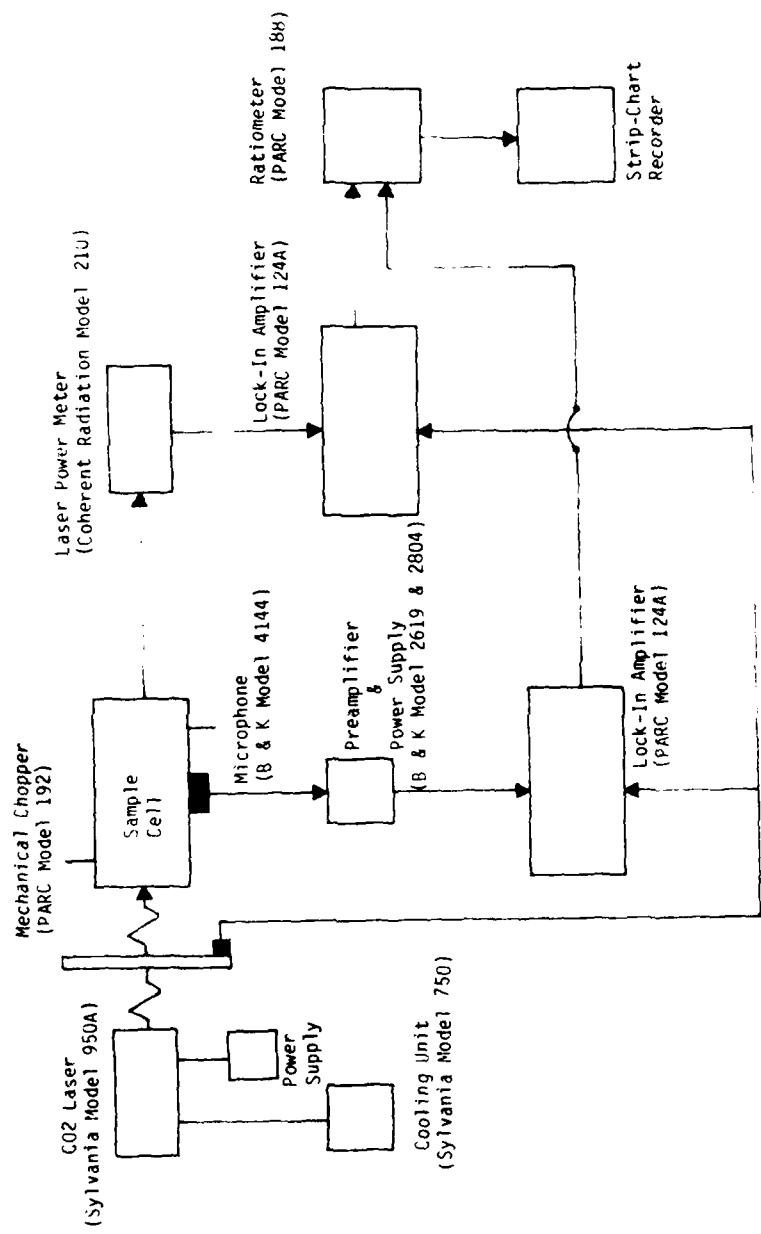


Figure 10. Optoacoustic spectrometer component integration for the measurement of the hydrazine fuels.

TABLE 10. RELATIVE ULTRASOUNDIC SPECTROMETER EQUIPMENT COSTS

<u>Component</u>	<u>Cost (1979)</u>
CO <sub>2</sub> Laser and Power Supply (Sylvania Model 950A)	\$16,480
CO <sub>2</sub> Laser Cooling Unit (Sylvania Model 750)	\$ 1,725
Variable Speed Chopper (PARC Model 192)	\$ 1,850
Microphone (Brüel & Kjaer Model 4144)	\$ 505
Microphone Preamplifier and Power Supply (Brüel & Kjaer Models 2619 & 2804)	\$ 1,173
Laser Power Meter (Coherent Radiation Model 210)	\$ 1,200
Lock-In Amplifier (PARC Model 124A; 2 Required)	\$ 9,570
Ratiometer (PARC Model 168)	\$ 1,740
Sample Cell (USAJAM Shop & Materials)	\$ 400
NET ESTIMATE (Dec 1979)	\$34,643

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